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PRINCIPAL CONTENTS IN THIS ISSUE:

Friction in Powder Metallurgy

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IT has been well said that the production of parts by powder metallurgy is an exact and painstaking process. There is no contradiction between the truth of this and the fact that mass production by powder metallurgy is possible and that thousands of parts per hour can be turned out to very close and stringent specification. Only those unacquainted with modern methods of mass production overlook the intense study of design both of parts and of the mechanisms which produce them, which precede any actual processing of material, and often the considerable research which is necessary before the production line can be developed.

The first step toward solving most modern problems in mass production is the breaking down, or analysing of the processes into units, each of which can be studied separately, and then when every aspect of the unit is known and understood, the work of building up, or synthesizing the complete process can begin. Such a procedure is as necessary in powder metallurgy as in any other mode of production. It begins with the preparation of the metal powders themselves, and the study of all the factors which can in any way affect their properties and the properties of the components made from them.

In like manner each succeeding step calls for study and understanding so that the processing of the material from powder to the finished article ready for market and use may proceed smoothly and efficiently. A factor which can play a part of outstanding importance in the pressing of compacts is friction, and its significance is not always given the attention it merits. The following notes on some of the more practical aspects of the subject may be of interest to all who essay the production of parts by powder metallurgy or who are users of parts so produced and to whom the information may be of help in diagnosing difficulties or troubles.

When metal powder, having been poured into a die, is pressed by the descent of the ram or punch into the die thus exerting pressure on the powder, friction can be engendered in the powder mass, that is inter-particle friction, and also between the walls of the die and the particles of powder ; this we can call wall friction as distinct from particle friction. A consideration of the many factors which play a part at this stage indicates clearly the complexity of the problems involved in so apparently simple a process as pressing, and can provide a useful exercise in the discussion and investigation of those elements that can make or mar success.

The first factor is the particle size and shape of the powder. With few exceptions the aim of pressing is to produce a coherent mass which shall have sufficient

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cohesion and strength to allow of essential handling between pressing and sintering. A step further, and it is a usual one, is to use such pressure as will give optimum density to the pressing. Obviously the particle size and shape will play a large part, also what we call the particle size distribution. True, if we have perfectly spherical particles all of one size we shall know what percentage of voids or porosity we can have with normal close packing, but as a rule we choose a particle size distribution such as to give us a minimum porosity and so a maximum density, especially where we desire the best physical properties attainable.

We also know that the particle shape of our powder can influence the ease or difficulty of pressing, can engender more or less inter-particle friction, just as the hardness or softness of the powder helps or hinders pressing by providing more or less resistance to the compacting pressure. The nature of the actual particles of metal will play a part, for one can readily understand that solid spherical particles of atomised metal will both behave and react differently to pressure than will the spongy irregularly shaped particles of metal reduced from oxide. Yet another variety of particle will be that produced by electrolytic deposition which so often has a dendritic or moss-like character.

So far we have considered only factors influencing inter-particle friction, and only certain aspects of those factors. If we are to have anything like a complete understanding of the part friction and inter-particle friction can play in the pressing operations of powder metallurgy we must go much further and think of whether lubrication in general of the whole mass of powder to be pressed in a die is going to be useful or detrimental in powder metallurgy. In considering inter-particle friction only, there is little doubt that the addition of a lubricant to the powder as a whole is inimical to obtaining the best results from pressing.

When pressure is exerted on the powder by the action of the ram or punch the first effect will be to crush or force the particles of powder closer together ; this means they will be rubbed together and it is now common knowledge that when that happens the points of contact or rubbing, even light rubbing, can and do rise to the temperature of the melting point of the metals. This rise of temperature is confined to an excessively thin layer of metal on the surface. It is known, as a result of the work of Bowden, Finch and others, that if conditions are favourable then the points of contact where such temperatures have been reached, can cohere. That, in fact, is the explanation and the mechanism of what happens when moving parts seize up. It can be combated to a very large extent by the use of lubricants. and wherever this contact smoothing or melting by friction or rubbing has taken place lubrication has a greater effect because of the smooth surface upon which the lubricant can form a thin film. But in powder metallurgy we

want the cohesive action to take place. That is the whole purpose of our pressing and later sintering. Why then reduce the efficiency of pressing and sintering by the use of lubricants on the mass of powder in dies.

If our reasoning is correct the less lubricant we add to our powder the better the result our pressing will give. We know there will be inter-particle friction, but that friction is playing a useful part for it is aiding the closer compacting of the mass in the die and also increasing the resistance of the pressing to damage by handling before sintering. There is one other aspect of the inter-particle friction that should be mentioned before we consider wall-friction and that is the effect of inter-particle friction on the distribution of pressure inside the die. It must never be forgotten that in pressing metal powders we never approach a hydraulic distribution of pressure where pressure is equal over the whole system. That is why one cannot have re-entrant angles in the design of parts to be produced by powder metallurgy. Metal powder does not flow, as plastics do during moulding, or as liquid metal does in injection moulding or die casting, and that limitation must never be forgotten. The nearest approach to flow with metal powders is obtained in certain types of hot pressing where indeed there is an appearance of flow, but the fact is negatived by the nature and quality of the physical properties that can be attained.

Wall-friction is in quite another category to inter-particle friction. It is almost always considerable, and has a large and important influence on the rate of compression and its effect on the compact. Lubrication, and efficient lubrication of the die walls is desirable in all cases. The condition of the die wall is of great importance from first to last. Smooth, highly polished die walls mean minimum friction during pressing with maximum effect for the pressure applied, whereas scored or worn die walls inevitably mean grave frictional losses. In this connection it may be mentioned that good American practice usually considers that wear on die walls aggregating to one thousandth of an inch should be a signal for repair of die by chromium plating and re-polishing.

Both outer-particle and wall friction can be influenced by the hardness, and to a lesser degree by the form of the individual metal particles comprising the powder and so where control can be exercised on these factors it may be used to minimise frictional effects where deleterious. Work hardening effects can be removed by judicious annealing and so too can the effects of oxidation which in some cases can materially increase the surface hardness of particles. Wherever work hardness, or hardness induced by any other factor is suspected, every available means should be taken to reduce that hardness before pressing takes place. If it is possible to do so the cause of the induced hardness should be removed, as this is preferable to conferring the obnoxious property and then eliminating it.

It will be obvious that where a small compression ratio exists, that is the ratio between the unpressed powder in the die, and the pressed compact, inter-particle as well as wall friction will exert a lesser effect than in cases where the compression ratio is large. In general a compression ratio of about 3 : 1 is aimed at, that is the height of the column of unpressed powder in the dies is three times the height of the pressed compact. Where it is as high as 4 : 1 even simultaneous top and bottom application of pressure will leave a pressure gradient in the pressing which will have the effect of giving high hardness and density values at top and bottom of the pressing and lesser values at the centre. If inter-particle friction is great then this effect will be accentuated, and still more so if accompanied by notable wall friction. This naturally affects the general physical properties of the pressing and such effects have been the cause of many failures with components produced by powder metallurgy, not because the process was unsound in itself, but because all the factors capable of influencing the results had neither been understood nor their significance taken into account.

Conditions arising from excessive friction during pressing, whether inter-particle or wall friction, not only produce differences in hardness and density in the pressed compacts, but may cause further and serious trouble during sintering. As an example the effect of porosity on decarburisation in the case of iron-graphite compacts may be cited. It is well known that decarburisation varies with the degree of porosity of compacts, other factors being equal. Hence the centre of a compact of less density and so greater porosity than the two ends would tend to decarburise to a greater extent in the centre with corresponding falling off in hardness as well as other physical properties.

Variations in the degree of shrinkage or swelling due to similar variations in density or porosity can also take place, all of which emphasises the value and the importance of careful attention to such factors as can affect friction either between the particles of powder in the die or at the die walls. The fact that what appears to be a very simple and perhaps somewhat obscure phenomenon connected with the nature of the powder in the die and the effects taking place during its compression, can profoundly affect the properties of the finished product is one more example of the fact that powder metallurgy is an exact process and that experience can only be acquired the hard way. Possibly the foregoing notes on friction may smooth the path for some newcomer.

School for Gas Turbine Technology

POWER JETS (Research and Development), Ltd. has taken over the School of Gas Turbine Technology at Ladywood Works, Lutterworth, previously run by the National Gas Turbine Establishment with conspicuous success. The School is closed until the end of May for reorganisation, the complete revision of the syllabus, and the preparation of new lectures for courses in industrial gas turbines and kindred subjects.

It is proposed to have academic courses for graduate engineers, as before. It is felt that there is room for some degree of specialisation, for instance, in the various specific fields of compressor theory and design, combustion, etc., for which a demand exists but is difficult to assess. It is also proposed to arrange practical courses for draughtsmen, testers, engineers and operators, depending upon the demand.

It should be noted that there is no profit motive represented in the operation of the School, the object of which is mainly to meet the wide public need for accurate and sound instruction in gas turbine technology. Enquiries and suggestions are sought which would assist in determining the demand for such specialised or practical courses : they should be addressed to Power Jets (Research and Development), Ltd., 8, Hamilton Place, London, W. 1.

Influence of Various Factors on the Creep of Lead

By J. Neill Greenwood, D.Sc., M.Met.E.* and J. H. Cole, M.Sc.†

Results are given of some long time creep tests on pure lead, containing 0·009% total impurities. They are of technological rather than scientific importance and should be useful in checking the results of previous workers who have predicted long time results from relatively short time tests. The results will prove useful to chemical engineers who use lead as a structural material.

Introduction

IN a recent article[1] the authors recorded some results obtained on various industrial leads under stresses of 350 and 500 lb. per sq. in. It is now proposed to give the results of some long time creep tests on a pure lead (U) containing 0·009% total impurities. This is the same lead which formed the basis of the alloys used in previous investigations and results on which were incorporated in Table I of the article cited.

The experiments fall into three groups :—

(a) The influence of steady stress at ordinary temperatures.
(b) The influence of steady stress at 50° C.
(c) The influence of steady stress and previous heat treatment of the lead, at ordinary temperatures with a fluctuating tensile stress imposed on the steady stress.

The conditions of preparation were as previously described[1], and the grain size was 0·2/0·5 mm. diameter or 50 to 200 crystals in the cross section of the test piece.

The results here recorded are of technological rather than scientific importance. They may be useful in checking the results of previous workers[2, 3] who have predicted long time results from relatively short time tests of 2,000 hours. An attempt is made also to guide those chemical engineers who use lead as a structural material, and to assess those features which should be taken into account in structural design. In this connection it should be noted that much of the American work has been done in connection with cable sheathing failure and the mode of preparation of test pieces (by flattening cable sheathing) almost precludes the use of this data in connection with rolled sheet.

Unfortunately it appears that there is no short time test for lead, which is comparable with the tensile test normally used to evaluate the strength of materials of engineering construction. The authors[1] have suggested that a comparatively short time test of 100 days' duration under a stress of 500 lb. per sq. in. might serve to classify leads or alloys. That is obviously a necessary preliminary step, but one which must be followed by quantitative data for lower stresses if structural design of lead vessels is to be placed on a better basis than seems to exist at present.

Influence of Stress at Ordinary Temperature

The specimens were subject to direct tensile stress by hanging a dead load through a spring to avoid any shock loading. The strain was measured with a Cambridge travelling microscope, the distance apart of two lines scribed on chrome plated strips soldered to the two ends of the gauge length. In the case of 200 lb. per sq. in. stress and lower, this method was not sufficiently sensitive and a simple 10 : 1 lever system was used to magnify the extension. The temperature during the first two years was maintained between 18 and 20° C. but during the war years this control lapsed and the laboratory temperature fluctuated between 14 and 24° C. For six months in each year, however, the temperature would remain between 18° and 20° C.

The results are given in Table I.

TABLE I.—PERCENTAGE INCREASE IN LENGTH AT 18° C. U LEAD STRIP ANNEALED 15 MINS. AT 100° C.

Stress lb./sq. in.	Duration of steady stress (years).			
	1	2	3	9
200	0·2	0·35	0·45	2·0
250	0·4	0·95	1·2	2·7
300	1·15	1·9	2·4	5·4
350	6·0*	9·4	10·4	—

* This specimen had begun to recrystallise at this stage. If no recrystallisation had occurred the extension would have been 5·0%.

The results are plotted in Fig. 1 as creep-time curves and in Fig. 2 as total creep in one, three and nine years respectively against stress. It will be noted that there is a marked increase in rate of strain between 250 and 300 lb. per sq. in. stress. This feature has been noted by other investigators.[4]

Influence of Stress at 50° C

For this series the specimens were hung as previously, but they were in an enclosure heated by two tubular resistors. The temperature was controlled by a mercury thermostat and relay and was kept at 49° ± 1° C.

The method of preparation and grain size were the same as in the previous series.

The results are given in Table II.

TABLE II.—PERCENTAGE INCREASE IN LENGTH IN ONE YEAR.

Stress lb./sq. in.	Temperature	
	50° C.	18° C.
150	1·15	—
200	1·35	0·2
250	1·6	0·4
300	4·6	1·15
350	7·6	6·0

After 300 days the temperature was allowed to fall to normal and the results given have been obtained by extrapolation of the creep curves so as to form a better comparison with those in Table I. The results are plotted in Fig. 3 from which it will again be seen that there is a marked change in rate of creep with stress,

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1 J. Neill Greenwood and J. H. Cole, *Metallurgia*, **36**, pp. 233.
2 H. F. Moore, B. B. Betty and C. W. Dollins, *Univ. of Ill. Bull.*, vol. XXXV, No. 102.
3 H. J. Phillips, *Proc. Hon. Soc. T. Mat.*, **36**, Pt. II, p. 170.

4 K. von Hanffstengel and H. Hanemann, *Zeit. Metallkunde*, **30** (1938), p. 4.
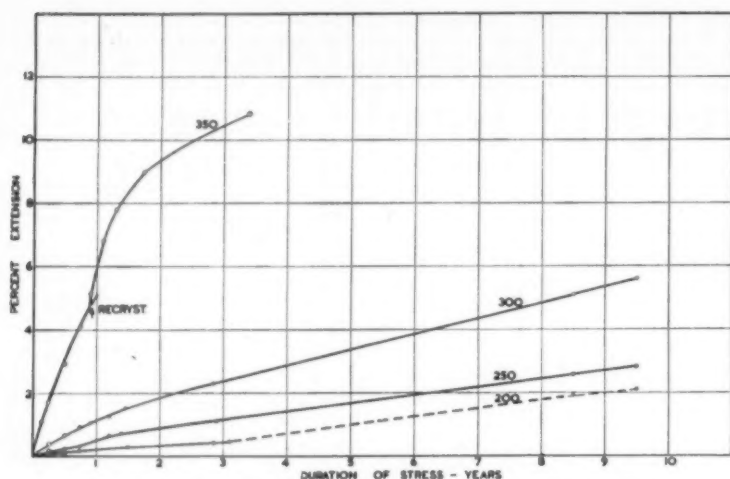
Fig. 1.—" U " lead annealed 100° C./15 min. Grain size
0.2/0.5 mm. Influence of stress at 15/24° C.

Fig. 2.—" U " lead annealed
100° C./15 min. grain size
0·2/0.5 mm. Temp. 15/24° C.

Extension after varying periods :—
A after 1 year
B ,, 3 years
C ,, 9 years

this time occurring at 250 lb. per sq. in. stress. The curve for 18° C. has been added for comparison purposes.

The same specimens were allowed to remain under stress at ordinary temperatures for a further 8½ years. The results of this period are given in Table III in which for comparison are given the corresponding figures from the previous series. That is, in both cases, the values given represent the total extension in 9½ years less the extension after 300 days at either 50° C. or 18° C. It is interesting to note that for each stress the creep rate is less after the initial period at 50° C. than that following the same period at 18° C., but it is doubtful whether this has any significance.

TABLE III.—PERCENTAGE EXTENSION DURING 8½ YEARS AT 18° C. OF SPECIMENS
PREVIOUSLY STRESSED 300 DAYS AT 50° C. AND 18° C. RESPECTIVELY.

Stress lb./sq. in.	Elongation during 8½ years	
	Previously at 50° C.	Previously at 18° C.
150	1·3	—
200	0·8	1·9
250	1·8	2·4
300	3·4	4·6

The Influence of a Superposed Vibratory Stress

Most creep tests have been reported on results obtained by dead load stressing, although, in some of the earliest work on cable sheathing, L. Archbutt[5] subjected some of his specimens to vibration, and found an increase in the rate of creep. The conditions obtaining in lead acid chambers are substantially quiescent, but this is not so when moving machinery is concerned. For example, the lead sheet casings of fans moving corrosive gases are liable to considerable vibration, and are known to fail by intercrystalline cracking.

As it was known[6] that in fatigue tests on lead the fracture is intercrystalline, it was thought that interesting and useful results would be obtained if a vibratory stress were to be superimposed on a steady stress obtained by dead loading.

An arrangement was constructed whereby the bars from which the specimens were suspended were in turn suspended from a floating platform which carried a ¼ h.p. motor driving a disc by means of a V belt. This
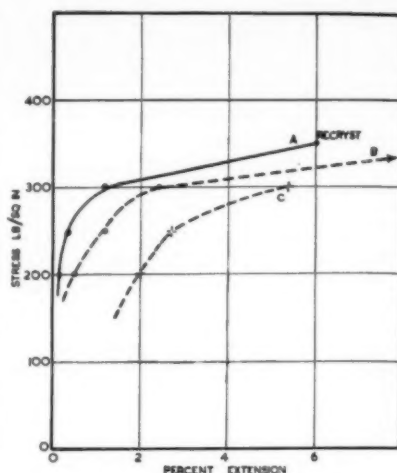
5 L. Archbutt, Trans. Far. Soc., 17, 1921, p. 22.
6 S. Beckinsale and H. Waterhouse, J. Inst. Met., 39, p. 375.

disc rotated at 3,000 R.P.M. and the motion conveyed a 50 cycle vibration which had a vertical component of approximately 0·05 mm. measured at the specimen suspension bar. The arrangement is shown in Fig. 4. The vibration was of course not simple, and observation showed that approximately once in three seconds the vertical amplitude increased to 0·1 mm. Further, as the dead loads were applied to the specimens through springs, these loads themselves were set in motion with a frequency of about 200 per min., the vertical amplitude being of the order of several millimeters. There was, therefore, nothing reproducible or known regarding the frequency or magnitude of the fluctuating component of the load. It is felt, however, that specimens were subjected to the same order of stress fluctuation provided they were under the same steady stress. To check this, two specimens under the same nominal stress which were found to be elongating at widely differing rates, had their positions on the suspension bar interchanged. This did not affect the rate of creep of either and this was taken as evidence that all positions on the suspension bars were subject to the same overall vibration characteristics. For the taking of readings it was necessary to stop the vibrator.

As it was known from other experiments that lead which had been annealed for 24 hours at 120° C. is more susceptible to intercrystalline cracking than it is in either the " as rolled " or annealed 15 min. at 100° C. conditions, two series of specimens were included in the test :

Series A—annealed 15 min. at 100° C. after rolling.
Series B—annealed 24 hrs. at 120° C. after rolling.

The average grain size of series A was about 0·5 mm. and series B about 0·7 mm. diameter.

The vibration was maintained for approximately two years and then the specimens were left under steady stress for a further 8½ years.

As in previous experiments the results in series A are complicated by recrystallisation (and consequent increase in grain size). It was found that vibration accelerated this recrystallisation.
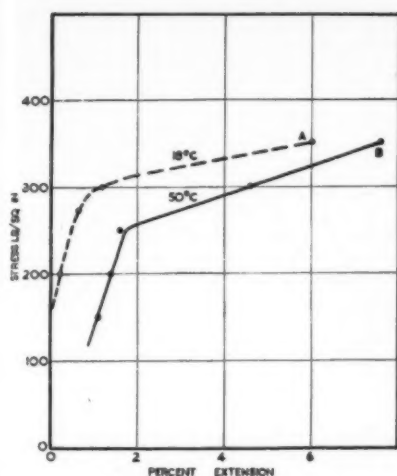
Fig. 3.—" U " lead annealed 100° C./15 min. Grain size 0·2/0·5 mm.
Extension after one year, A at 18° C., B at 50° C.
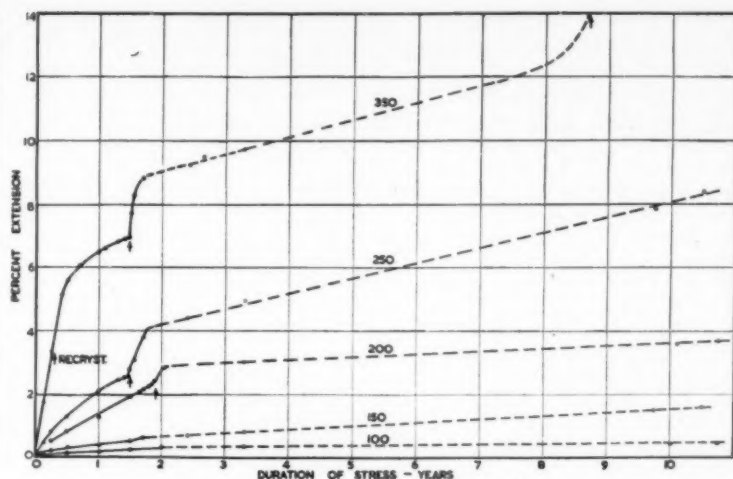
Fig. 5.—" U " lead annealed 100° C./15 min.
Influence of stress with vibration 2 years, then steady stress 8 years—15/24° C.

The results are given in Tables IV and V; and are plotted in Figs. 5 and 6.

In Fig. 5 the curves for the vibration period are in full line and for the period without vibration in broken line. Since the vibration increased the rate of creep (compare Tables I and IV) there is a distinct deviation in the curves corresponding with the cessation of vibration. It will be noted that the change in rate is not a simple function of stress. For example the rate of creep under steady stress is approximately the same at 200 as at 150 lb. per sq. in. and at 250 is the same as at 350 lb.
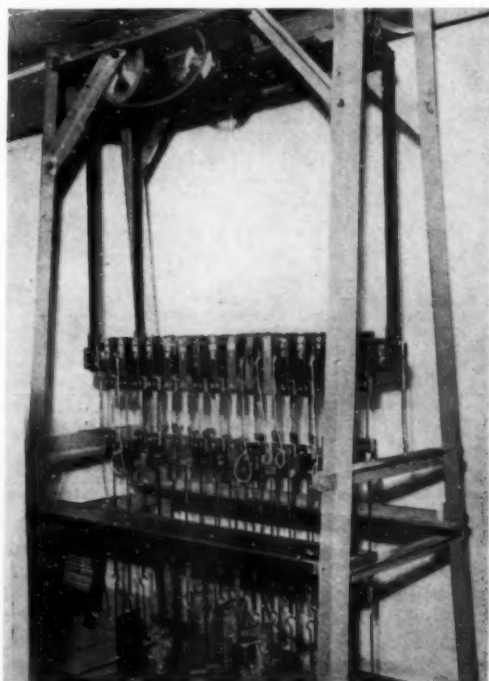
Fig. 4.—Arrangement for vibrating creep specimens.

TABLE IV.—PERCENTAGE EXTENSION UNDER LOAD. U LEAD SERIES A.

| lb./sq. in. | With vibrator | | | Without vibrator |
| | 1 year | 2 years | | 8½ years |
	Actual	Actual	Extra-polated*	Actual
100	0·2	0·35	—	0·1
150	0·4	0·6	—	0·95
200	1·4	2·8	2·5	0·9
250	2·1	4·7	3·0	4·2
350	6·5†	9·2‡	7·2	Broke after further 6½ years with 20% elongation.

* These values are obtained by extrapolating the creep curves along the path taken prior to recrystallisation.
† This recrystallised after 80 days and 2·4% elongation. Extrapolation is therefore impracticable.
‡This specimen recrystallised again after 530 days and 6·8% elongation.

TABLE V.—PERCENTAGE EXTENSION UNDER LOAD. SERIES B.

| Stress lb./sq. in. | With vibrator | | Without vibrator |
	1 year	2 years	8½ years.
100	0·1	0·15	0·15
200	0·4	0·95	1·75
350	2·4	4·0	Broken after further 5 years with 11% total elongation.

per sq. in. In the vibration period the deviations marked by arrow heads are due to recrystallisation—this phenomenon being accompanied by a marked increase in creep rate. The first recrystallisation under 350 lb. per sq. in. is accompanied by a marked deviation when the curve is plotted to a different scale.

In Fig. 6 curve A corresponds with curve C of Fig. 2 but the extension plotted is for 8 years instead of 9 years. Curve B by comparison with curve A indicates the increased creep rate during the first two years caused by vibrations and curve C, which relates to the second stage of 8 years without vibrations, is substantially similar to Curve A, particularly for lower stresses.

As regards the two series A and B, comparisons of Table IV and V shows that in the vibration period at each corresponding stress the specimens annealed at 125° C. for 24 hours extend appreciably less than do those annealed 100° C. for 15 min. In the following period without vibration the reverse is true.

Discussion of Results

(1) *Influence of stress at 18° C (65° F).*

It will be seen from Fig. 2 that the creep rate of this lead increases markedly in the range 250/300 lb. per sq. in. This feature was previously noted by Hanffstengel and Hanemann[4] who gave a value 165 lb. per sq. in. at 25° C. for the transition stress. This might be described as a "creep yield point" and is probably due to a relatively sudden increase in the rate of plastic yielding or crystalline slip. At lower stresses creep probably consists essentially of viscous flow.[7] The determination of this stress might be considered comparable with the yield stress in steel and would serve as a guide to the absolute upper limit of stress permissible in structural design. In this case the creep yield stress at 18° C. is between 250 and 300 lb. per sq. in. though it becomes less definite as the duration of stress increases. It is evident that for use under quiescent conditions at, say, 15/20° C. pure lead of this grade should therefore not be stressed beyond 250 lb. per sq. in., when an extension of the order of three per cent in 10 years is to be expected.

(2) *Influence of stress at 50° C. (120° F.)*

From Fig. 3, it is noted that the same type of relationship holds, but as the tests were only continued for 300 days, extrapolation is necessary to give a comparable value to that quoted above. This is unsatisfactory even though the creep curves (up to 300 lb. per square inch) showed a linear relationship between extension and time. However, keeping in mind the limitations mentioned, it can be stated that in one year at 50° C. (120° F.) one per cent. extension would be expected in this lead with a stress of 140 lb. per sq. in. The creep yield stress as defined above is 250 lb. per sq. in.

In Fig. 3, the two comparable curves for extension at 18° C. and 50° C. have been included. Very approximately it can be said that raising the temperature 30° C. necessitates lowering the stress by about 150 lb. per sq. in. in order to obtain similar extensions in a given time. This refers to stresses which as defined above may be suitable for structural design, that is, are below the creep yield stress, and shows how sensitive lead is to operational conditions.

(3) *Influence of vibration at ordinary temperature.*

The relationship between extension after one and two years and the applied stress, as shown in Fig. 7 is of the same general type as that in Figs. 2 and 3, but the transition between low and high creep rates is not well marked. Comparison with Fig. 2 shows that the fluctuating stress system imposed on the steady stress necessitates lowering the latter by about 100 lb. per sq. in. to obtain similar creep rates.

(4) *General features associated with creep under vibratory conditions.*

(a) Each specimen has been examined with a binocular

7 D. Hanson, *Metals Technology*, 1939.
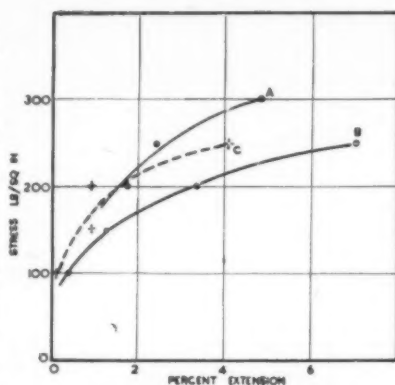
Fig. 6.—"U" lead annealed 100° C./15 min. Grain size 0·2/0·5 mm.

A : Extension after 8 years' steady stress.
B : Extension after 8 years of which two years were with vibration.
C : Extension after 8 years steady stress following two years with vibration.
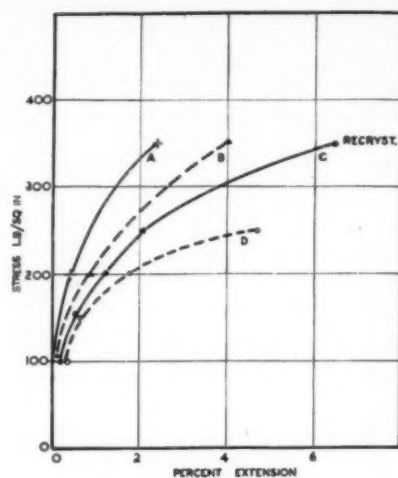
Fig. 7.—"U" lead annealed 100° C./15 min.

A : Extension after 1 year. Annealed 120° C./24 hours.
B : Extension after 2 years. Annealed 120° C./24 hours.
C : Extension after 1 year. Annealed 100° C./15 min.
D : Extension after 2 years. Annealed 100° C./15 min.
Temp. 18° C.
Steady stress with vibration superposed.

microscope at the end of 10½ years under stress before and after re-etching. Only in the case of two specimens stressed at 350 lb. per sq. in. was intercrystalline cracking noted. One of these had been annealed for 15 minutes at 100° C. and had recrystallised in large grains during the test. The other had been annealed at 120° C. for 24 hours and had not recrystallised. Both had broken with a marked intercrystalline fracture, the former after 8¾ years with 20% elongation and the latter after 7 years with 11% elongation. It is important to realise that the ductility of lead as measured by elongation is markedly less when fracture occurs under prolonged stress conditions. It has been shown[8] that under certain conditions lead will recrystallise under stress. In our observations this has always been accompanied by a considerable increase in grain size.

(b) Vibration causes an acceleration of this recrystallisation. The following values illustrate this point ; and it is confirmed by observations on a still purer lead.

TABLE VI.—Extension Required to Cause Recrystallisation Under Stress at Ordinary Temperatures (15-20° C.)

Stress lb./sq. in.	Per cent. elongation when creep curve reveals recrystallisation	
	Without vibration	With vibration
200	—	2·4
250	—	2·6
300	Greater than 5·6 if at all	—
350	4·7	2·4 (6·8)*

* A second deviation corresponding to recrystallisation occurred in this case.

Two specimens were undergoing recrystallisation when the vibration stage was stopped after about two years. These were the specimens stressed at 200 and 250 lb. per sq. in. respectively. The increased creep rate accompanying recrystallisation is clearly seen on the two curves in Fig. 5 at the positions marked by the arrow heads. With the cessation of the vibratory stress the recrystallisation did not progress and when examined at

8 J. Neill Greenwood and Howard K. Worner, *J. Inst. Met.*, **64**, 135.

the end of 10½ years it was found that only about half of the gauge length was recrystallised. This is clear confirmation of the accelerating effect of vibration.

(5) Comparison with results of other workers.

Moore, Betty and Dollins[2] published some charts relating *inter alia* to tensile extension of several industrial leads. The specimens were cut from cable sheathing and therefore both the method of fabrication (extrusion) and the preparation of the material for test were widely different from those pertaining to the experiments described herein.

The results for two leads at three temperatures are given in Table VII. In order to compare them with those previously given they have been reduced to the basis of percentage extension in one year.

TABLE VII.

(MOORE, BETTY AND DOLLINS). CREEP OF LEAD CABLE SHEATHING.

Stress lb./sq. in.	Percentage extension in one year					
	Grade III lead*			Grade II lead 2G†		
	78° F.	110° F.	150° F.	75° F.	110° F.	150° F.
50	0·03	0·06	0·08	—	0·03	0·045
100	0·07	0·13	0·28	0·035	0·065	0·16
150	0·14	0·23	1·4	0·07	0·15	0·4
200	0·24	0·60	—	0·12	0·25	—
250	0·50	1·70	—	—	—	—
	26° C.	43° C.	66° C.	24° C.	43° C.	66° C.

* Total impurities 0·08% of which 0·07% is Bismuth.
† Total impurities 0·11% of which 0·056% is copper, and 0·043% is bismuth.

From these results it will be seen that these leads with greater impurity content creep at a slower rate than does the lead which forms the basis of the present paper. However, the test specimens were taken from sheath which had been flattened and therefore cold worked to an unknown extent. From previous work in the University of Melbourne laboratory[8] it would appear that this cold work rather than the impurity content is responsible for the lower creep rate.

Gohn, Arnold and Bouton[9] give some results on long time creep tests for both high purity lead and "chemical" leads, and for several lead alloys. Results are given for specimens cut from cable sheaths and from extruded "tapes." The merit of this work lies in the length of time over which measurements were made. On the other hand there was no attempt at accuracy of measurement or detailed following of the behaviour of the different alloys. The results also suffer in part from the mode of preparation of test pieces, namely by flattening cable sheathing stripped from the cable. This leaves the test pieces in an indeterminate state from the point of view of cold working and as previously stated creep rate is very sensitive to small amounts of deformation. Gohn, Arnold and Bouton rightly draw attention to the necessity for prolonged tests at low stresses for in these the phenomena such as recrystallisation which tend to complicate the results are not introduced. However, from Fig. 1 it will be seen that for stresses below 300 lb. per sq. in. with pure lead, it would be necessary to continue the tests for at least three years to be able to extrapolate to ten years. Even so, there is no certainty that the extrapolation will agree with the actual extension if measured over the longer period. This also is illustrated in Fig. I. The curve for 200 lb. per sq. in. stress extrapolated after 3 years indicates an expectation of an elongation of 1% after 9½ years, whereas the

9 G. R. Gohn, S. M. Arnold and G. M. Bouton, *Proc. A.S.T.M.*, **46**, p. 990.

measured elongation was 2%. With stresses of 250 and 300 lb. per sq. in. respectively extrapolation was satisfactory.

A few values given by Gohn, Arnold and Bouton are comparable with those given in the present paper. For example, for high purity lead extruded tapes extensions of the order of 1·5% were obtained in 8 years under stresses of 100 and 150 lb. per sq. in. In Fig. 6 results on U lead are given, extensions after 8 years for various conditions being plotted against stress. It will be seen that values of the order of 1% extension are indicated for a stress of 150 lb. per sq. in.

Summary

The data obtained relate to a commercially pure lead (U) in the form of rolled strip lightly annealed and with a grain size about 0·5 mm. diameter.

(1) At 15/20° C. this lead stretched at the following rates :—

Stress						Rate of stretch (over 9 years)
*150 lb./sq. in.	..	..	..	..	..	0·15% per annum
200	„	„	..	..	..	0·22% „ „
250	„	„	..	..	..	0·30% „ „
300	„	„	..	..	..	0·40% „ „

(2) At 50° C. the same lead behaved as follows :—

Stress						Stretch in one year
*50 lb./sq. in.	..	..	..	..	..	0·4%
*100	„	„	..	..	..	0·7%
150	„	„	..	..	..	1·15%
200	„	„	..	..	..	1·35%

*(3) (a) When a gentle 50-cycle vibration was superposed on the steady stress the following average rates of stretch were obtained :—

Stress						Rate of Stretch (over 2 years).
100 lb./sq. in.	..	..	..	..	..	0·17% per annum
150	„	„	..	..	..	0·30% „ „
200	„	„	..	..	..	1·4% „ „
250	„	„	..	..	..	2·3% „ „

(b) When the vibratory stress was removed the following average rates of stretch were observed :—

Stress						Rate of Stretch (over 8½ years)
100 lb./sq. in.	..	..	..	..	..	0·012% per annum
150	„	„	..	..	..	0·11% „ „
200	„	„	..	..	..	0·12% „ „
250	„	„	..	..	..	0·5% „ „

(4) When the lead was annealed at 120° C. for 24 hours, a marked stabilisation of the crystal structure occurred. After this treatment the following rates of stretch were observed :—

(a) With the 50 cycle vibration :—

Stress						Rate of Stretch (over 2 years)
100 lb./sq. in.	..	..	..	..	..	0·07% per annum
200	„	„	..	..	..	0·47% „ „

(b) After the vibratory stress was removed :—

Stress						Rate of Stretch (over 8½ years)
100	..	..	..	..	..	0·02% per annum
200	..	..	..	..	..	0·2% „ „

* These values are obtained by extrapolation.

(5) There appears to be a stress, referred to as the creep yield stress, above which there is a marked increase in the rate of creep. For this lead (U) the values obtained were :—

Temperature					Creep yield stress
15/20° C.	..	..	..	..	300 lb./sq. in.
50					250 „ „

The significance of this will be considered elsewhere.

These experiments were carried out in the Rosenhain Memorial Laboratory.

In a later article it is proposed to consider results obtained with some lead alloys.

The Brittle Lacquer Method of Determining Stresses

The lacquer method of assessing the magnitude and positions of strains and corresponding stresses is briefly described ; compositions of brittle lacquers are given and some of their properties are discussed. Lacquer coatings must be continuous and an electrometric method of determining continuity is described. Some examples of this form of test are given.

THE lacquer method of assessing the magnitude and positions of strains and corresponding stresses in metal parts originated with Dietrich and Lehr of the German firm Maybach in 1932. It consists in the application to the surface of the part of a thin film of a special lacquer, sufficiently elastic to follow the deformation of the article on the application of an increasing load, but sufficiently brittle to develop cracks at a certain degree of strain within the elastic range of the metal. The cracks make their appearance first in those places where there is the greatest stress concentration, and, then, as the load is increased, in places of progresively lower stress concentration. Thus the positions of greatest danger in service are revealed.

It has been established that the cracks in the coating are at right angles to one of the principal stresses, viz., to the one of greatest absolute value. The cracks are, therefore, tangential to the second principal stress (in a surface, of course, the third principal stress does not exist). If one has a picture of the cracks obtained under working loads, one can, accordingly, draw the trajectories of principal stresses existing on the surface of the sample being tested. It is particularly useful for the study of articles of complicated pattern, where mathematical analysis is almost impossible.

In the main, the method is restricted to the study of tensile stresses. Only badly defined creases, which often disappear when the load is removed, are found in places of compression. Modifications, however, allow compressive stresses to be determined. Thus, the article may be subjected to a suitable degree of compression within the elastic-limit, then coated with lacquer, and left to dry while the load is maintained. When the load is removed, cracks appear in a direction perpendicular to the principal compression stresses. Alternatively, the article may first be coated with lacquer, then loaded slowly to some pre-determined degree of compression so that no notable changes occur in the lacquer coating, and finally so rapidly unloaded that the coating cannot keep pace with the rate at which the sample returns to its original dimensions, thus producing cracks in places of greatest compression.

Applications have been found in torsion and bend testing. Pure torsion of a rod causes cracks to appear at an angle of 45° to the axis of the rod.

Quantitative analysis of stresses has also achieved some success by this method. Here, it is very necessary to use lacquers of well-defined properties, under definite conditions of temperature, humidity and pressure.

Basic Requirements and Composition of Lacquers

The success of the brittle lacquer method depends on the choice of a stable lacquer, its correct application on the surface to be studied, the care employed in preparing the surface, and the possibility of creating loading conditions similar to those to which the part will be subjected in service.

The lacquer should adhere well to the surface, forming a single unit, as it were, with the sample. For this, it is essential that all rust, oxide, dirt, etc., be removed, perhaps by treatment with hydrochloric acid, followed by alkali. Also, it must be remembered that the degree of adhesion depends on the composition of the lacquer and the drying conditions after application.

The lacquer must show a brittleness sufficient for cracks to be formed in it at stresses below the elastic limit of the material of the article. It should possess, therefore, a high modulus of elasticity, and a small extension under tension. If the lacquer is insufficiently brittle, cracks may not appear at all, or only after the article has been taken beyond its yield point.

The lacquer should be reasonably transparent and possess the maximum mechanical stability. Its transparency assists in checking the adhesion and improves the visibility of the cracks. Mechanical stability ensures confidence in the results obtained.

Prior to the introduction of this method there existed certain somewhat similar methods of studying stresses. For instance, with parts subjected to rolling, scale is thrown off from the places of greatest stress, and with polished steel parts under strain, Lüders lines appear. Sometimes a thin layer of a cement solution or shellac has been applied to a sample for the purpose of revealing the Lüders lines more clearly. All these phenomena, however, occur only when the metal is taken beyond its yield point ; thus, they are unsuitable for the study of objects working within the elastic range.

Descriptions of the lacquer method given by foreign investigators have been limited, so far, to an account of the results obtained. Details of the lacquer composition, technique of application, etc., are omitted.

Attempts by Russian workers, including the present author, to devise suitable lacquers for the purpose have shown that a number of different lacquers may be used successfully. The following are some of the most effective :—

(1) Colophony (50 g.) and celluloid (5 g.) in alcoholic amyl acetate (100 c.c.).
(2) 50% solution of Albertol in xylene.
(3) 50% solution of colophony in methyl alcohol.
(4) 50% solution of colophony in acetone.
(5) 50% solution of Iditol in methyl alcohol.
(6) 50% solution of Iditol in acetone.
(7) 50% solution of colophony and Iditol in various proportions in methyl alcohol.

Colophony and ester gum are examples of the more brittle lacquers. If a lacquer is too brittle, the brittleness may be reduced by adding from 1 to 5% of paraffin.

Some of the Properties of Lacquers

Apart from the recording of stress distribution and the revealing of zones of stress concentration, the possibility of quantitative evaluation of stresses is an attractive feature of the lacquer method. In Russia, this problem has been examined by workers at Leningrad University, and Fisher and Shikhobalov attempted to find a lacquer that would give, at normal temperatures, visible cracks on the attainment, in a steel rod under tension, of a stress of 40 kg. per sq. mm., with a maximum error of ± 10%.

They studied matt lacquers from nitro-cellulose and celluloid, bakelite lacquers, and transparent lacquers from nitro-cellulose, colophony and celluloid. The matt lacquers were found unsuitable because of difficulty in seeing the cracks, and the bakelite lacquers were often too brittle and their application to a metal surface caused trouble. They obtained best results with a lacquer of the composition : 100 c.c. of alcoholic amyl acetate, 50 g. of colophony, and 5 g. of celluloid. With this lacquer 40 experiments were carried out. In 30 cases cracks developed at a stress of 40 kg. per sq. mm., and in the other cases, the maximum and minimum values differed from this figure by 27·1 and 25%, respectively.

Although the results appeared very hopeful, subsequent work by Fisher himself, Prokofev, Makarov, the present author, and other investigators showed that there were various difficulties in the way of obtaining quantitative results.

Prokofev studied lacquers of Albertol in xylene, colophony and glycerine ester gum, and copal, and also colophony containing 1 to 5% of paraffin. The albertol lacquer appeared more suitable for revealing zones of stress concentration than for quantitative work. A colophony lacquer with 1% of paraffin, applied to a metal sample, gave the first cracks at the following stresses :—

Tension .. 17·8 kg. per sq. mm. ± 8%
Bend .. .. 17·1 kg. per sq. mm. ± 4%
Torsion .. 15·7 kg. per sq. mm. ± 0·5%

With colophony containing 2% of paraffin, the first cracks appeared on metal at elongations of 42×10^{-5} ($+13\%$ and -11%) and on wood at $0 = 47·5 \times 10^{-5}$ ($+20\%$ and -10%).

Andreevsky used molten colophony at 135° C. to coat his samples, which were heated to 100° C. at the moment of application. He studied the effect of additions of paraffin. With more than 4% of paraffin, he failed to find cracks in the lacquer layer even under considerable deformation. With 1 to 3% of paraffin he obtained the results shown in the table.

COLOPHONY CONTAINING PARAFFIN.

Paraffin content (%)	Mean critical stress (kg. per sq. mm.)	Mean deviation of critical stresses	
		Absolute (kg. per sq. mm.)	Relative (%)
1	22·0	2·8	12·7
2	29·3	3·9	13·3
3	42·4	7·6	18·0

Andreevsky also studied the effect of various lengths of time between the termination of the drying period, in the case of 50% solutions of colophony in acetone and

the actual test. Two applications of the lacquer were made in each case, and the samples were heated for 1 hour in a thermostat at 160° C. after each application. The results showed that as the time of keeping was increased, the critical stress also increased, but tended towards a constant value.

A very detailed analysis of the results showed that atmospheric conditions (humidity, temperature and barometric pressure) had a pronounced effect on the mechanical properties of the lacquer, e.g., a 1·65-fold difference in mean critical stress for 10 samples could occur between days of high and low humidity. Similar results were obtained by the present author, who also noticed that cracks which had formed during a test tended to disappear after a while.

Electrometric Method of Determining Continuity of the Coating

The method of application used by the present author is as follows : the lacquer, such as a solution in alcoholic amyl acetate (100 c.c.) of colophony (50 g.) and celluloid (5 g.) is brushed onto the part, which is then dried in a thermostat at 59 to 80° C. for 20 to 30 minutes. A second coat is similarly applied and the sample is kept for 30 to 40 minutes at the same temperature as before. With a rapidly-solidifying lacquer, such as colophony with paraffin, ester gum, etc., the material is applied by brush to a surface heated previously to near the melting point of the lacquer, but in any case, not below 100° C. ; it is then left at 90 to 100° C. for 1 hour, and the operation repeated if necessary. If only zones of stress concentration are required, the temperature after application may be reduced to 60° C., and if the lacquer has been applied carefully, one coat is sufficient.

The brush method is superior to all other methods of application, dipping, spraying with powder followed by melting, and spraying with solution, but the succeeding process of heating is advisable to remove brush marks. Best results of all are obtained when the sample is heated beforehand.

In the case of single coats, it is possible that bare patches may remain. These gaps in the coating may be seen under a microscope, but are often difficult to discover by the unaided eye. Moreover, their presence distorts the picture of crack-distribution. It is, therefore, desirable to have available a method of checking the continuity of the coating, particularly so in the case of articles of complicated shape.
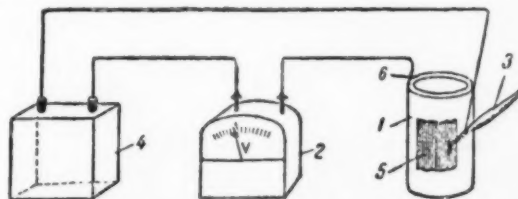
Fig. 1.—Diagram of defectoscope for studying continuity of lacquer coatings. 1—sample, 2—galvanometer, 3—brush, 4—accumulator, 5—lacquer film, 6—clamp.

For this purpose Yakubovich and Solovev have worked out a simple electrometric method. The apparatus is shown diagrammatically in Fig. 1. The sample (1), coated with lacquer (5), is connected through a sensitive galvanometer (2) to one terminal of a 4–6 volt battery (4), the other terminal of which is connected to a soft-hair brush (3). Before the test, the brush is

Fig. 2.—Cracks in the lacquer layer on two samples subjected to bend. Upper sample—wood, lower sample—steel.

moistened with a weak solution of an electrolyte, e.g., 0·1% sodiumchloride solution.

When the moist brush is applied to the surface no indication is given by the galvanometer needle except at a place where there is a break in the coating. The whole of the surface of even a complicated part may be examined quickly by this means.

Examples of the Use of the Brittle Lacquer Method

Various applications of the method and illustrations of the effects obtained have been given by Dietrich and Lehr, and by later investigators. The method, however, is given only in general terms, and hence it is difficult to submit the results to critical and comparative examination.

Fig. 2 shows the effect produced in test-pieces of wood and steel subjected to a bending test by means of loads applied at the middle. Figs. 3 and 4 show cracks in lacquer films applied to engine parts; static loading was produced in the directions shown by arrows.

Most of the lacquers, the composition of which is given above, will, when properly applied to steel (modulus of elasticity 20,000 kg. per sq. mm.), give the first cracks at stresses of about 20 to 40 kg. per sq. mm., corresponding to a relative elongation of 10^{-3} to 2×10^{-3}. This degree of elongation is attained, in the case of aluminium alloys (modulus of elasticity 7,000 kg. per sq. mm.) at stresses of 7 to 14 kg. per sq. mm., i.e., at stresses beyond the elasticity limits.

A special study of aluminium alloy parts has been made by the present author with a view to improving their design and construction. For this purpose, the most suitable lacquer was found to be pure colophony.
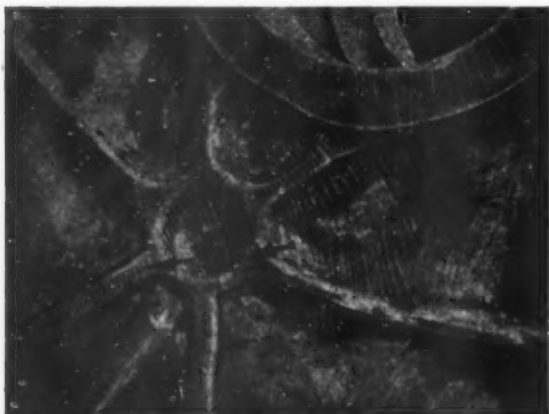
Fig. 3.—Cracks in the lacquer layer on engine parts under static loading.

Removal of volatile constituents by heating tended to stabilise all the varieties of colophony used, nine in all, in respect of brittleness, and reduced the scatter of results. The first cracks appeared at stresses of from 2 to 5 kg. per sq. mm. Cracks were most easily seen when the thickness of the coat was 0·2 to 0·4 mm., but they could be observed even when the thickness was only 0·05 to 0·1 mm. Colophony varies, however, so
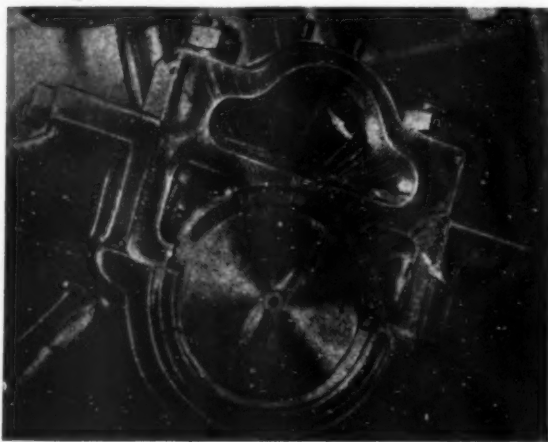
Fig 4.—Cracks in the lacquer layer on engine parts under static loading.

much in brittleness that it is always necessary to carry out a check on metals of known characteristics when a new batch is employed.

Samples were tested in tension, compression, impact, vibration, and fatigue. The results have been found most useful in revealing unsuspected places of weakness due to high stress concentration. In combination with tensometric method of measuring deformation it has considerably shortened the time required to obtain complete pictures on a quantitative basis of the stress distribution in complicated engine parts.

British National Committee for Crystallography

THE Royal Society, as the national body adhering to the newly-formed International Union of Crystallography has recently set up a British National Committee for Crystallography under the chairmanship of Sir Lawrence Bragg. The members of the Committee are : Professor W. T. Astbury, F.R.S. (Royal Society), Professor J. D. Bernal, F.R.S. (Royal Society), Mrs. D. C. Hodgkin, F.R.S. (Royal Society), Mrs. K. Lonsdale, F.R.S. (Royal Society), Sir George Thomson, F.R.S. (Royal Society) Professor C. E. Tilley, F.R.S. (Royal Society), Dr. G. M. Bennet, F.R.S. (Chemical Society), Mr. D. A. Oliver (Institute of Metals), Professor E. G. Cox (Institute of Physics), Dr. C. Sykes, F.R.S. (Iron and Steel Institute), Dr. F. A. Bannister (Mineralogical Society), Dr. H. Wilman (Physical Society).

In addition to the above, Professor P. P. Ewald, Dr. R. C. Evans and Dr. W. H. Taylor as members of the Provisional Executive Committee of the International Union are *ex-officio* members of the National Committee.

Plastic Deformation of Carbon Steels

By Richard Saxton

The most striking characteristic of cold-drawn carbon steels is their high tensile strength, but to obtain the best results necessitates a wide knowledge of the various qualities and their response to the stress imposed. Several factors involved are associated with the plastic deformation of the steel, some of the more important of which are discussed in this article.

THE plastic deformation or cold working of carbon steels in wire or bar form necessitates a wide knowledge of the various qualities and their response to the stress imposed. Uniform crystal flow under pressure induced is essential, otherwise cross-sectional stress is set up, leading to a brittle condition detrimental to further processing.

The reduction schedule is drafted in accordance with the response of the particular material to the pressure applied, and the aggregate drafts possible without detriment to the quality. The higher the carbon or manganese content the greater the resistance to deformation, both in single and aggregate draftings. Ductility is not a ruling factor, as many mild quality steels, in particular charcoal iron, are too mild to withstand the stress per draft possible with the harder qualities.

Preparation of Material

Preparation of the material for cold-work reduction necessitates removal of all scale and foreign surface matter ; the process being known as de-scaling or acid cleaning. To accomplish this, material in coil or bar form is immersed in a suitable acid-water solution, hydrochloric or sulphuric acids being the chief agents employed. The efficient removal of scale is essential, otherwise it is probable that any left adhering will be forced into the base metal during its passage through the reduction zone. Where this occurs a galvanic couple is set up, leading to electrolytic action and resultant corrosion. Scale, being cathodic to the metal surface, is unaffected, but corrosion is set up in the base metal.

Similar action has been noted with pitted surface defects. Minute traces of oxide or scale, not eliminated by acid processing, are retained in pits and rough surfaces. During reduction the surface metal is forced over these pits, forming what are known as " slivers." The resultant corrosion action causes these slivers to corrode and fall away, leaving a rough surface detrimental to further processing.

Following acid treatment and subsequent " baking " to drive off the acid in the form of occluded hydrogen embedded in pores of metal, the material is ready for the reduction process.

Reduction Process

The number of drafts and the percentage of reduction possible is dependent on the response of the quality to the aggregate pressure imposed. Where the material is of mild or medium quality and the finishing schedule necessitates a fair number of drafts, the general practice is to reduce by the continuous process. Such a process is illustrated in Fig. 1 which shows a continuous 4-hole drafting machine, reducing 5 S.W.G. (0·212 in.) mild steel material to 13½ S.W.G. (0·086 in.), and forming a 24 in. dia. coil. In the higher carbon qualities (0·75–
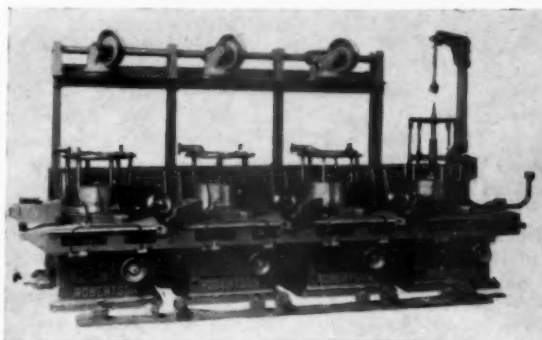
Fig. 1.—A continuous four-hole drafting machine for reducing 5 S.W.G. mild steel to 13½ S.W.G.

0·85% carbon), this machine would reduce to 11½ S.W.G. (0·110 in.). In Fig. 2 is shown a continuous machine reducing the 13½ S.W.G. from the previous machine to 21 S.W.G. in 5 drafts, and forming a 12 in. dia. coil. Further reduction is effected by a 9-hole drafting machine, shown in Fig. 3, which, if required, will reduce the 21 S.W.G. to 30 S.W.G. (0·0124 in.), and form a 6 in. dia. coil.

Reduction of the coil diameter as the material is cold worked finer is essential to retain its circular shape, as material in the hard condition is liable, if produced in larger diameter coils, to turn over on itself and form what is known in the Trade as a figure 8. Bent in this form it is practically unserviceable, and is usually consigned to the scrap heap.

As will be noted from a study of the illustrations, the material is passed through a reducing die, situated in the die holder on the base of the draw bench, around the drum for a number of turns, and finally wound off the top, round the pulley overhead and down to the succeeding drum, where the reduction operation is repeated. A special cage is mounted on the last or finishing drum, to facilitate withdrawal of the coil when necessary. As the back end of the coil, undergoing reduction, is reached, the commencing end of the next coil is welded to it to maintain continuity of process.

To facilitate the passage of the material through the die and reduce friction, a special type of dry lubricant is employed, known as " wire drawing " soap. The properties essential in a compound of this nature are efficient lubrication under high pressure, ability to withstand heat generated without detriment to properties, and affinity to combine with the elements employed as lubricant carriers, such as lime, etc.

Due to the pressure imposed, during travel through the die reduction-zone, certain fundamental changes take place in the material, independent of the reduction performed. First, the structure is transformed to a

tough, fibrous material ; the original grain formation is fragmented ; and crystallites are formed to orientate in one direction.

Research has revealed the effect of cold working or the cold plastic deformation of carbon steels, is to cause crystalline structure to assume a practically constant orientation. As a result of subjection to cold working all crystals tend to form a rhombic dodecohedral plane, perpendicular to the length of the material, with a cube face lying in the surface at all points, and it has been suggested by several authorities that reorientation is the cause of hardening in material subjected to cold plastic deformation processing.

Changes taking place in the metal structure under pressure are as follows : first, there is slip on the crystal cleavage planes, followed, as these harden, by slip between the crystals. Research on this action as shown when initial yield has taken place and the metal resists further yield, there is a proportional decrease in internal slip and an increase in external.

The speed at which carbon steels are cold worked in wire form is dependent on the carbon and manganese content : diameter of material ; and type of machine employed, but the average for mild steel quality— $0 \cdot 10\%$ carbon content—is 100–250 ft./min. in $\frac{1}{2}$–$\frac{1}{2}$ in. commencing diameters. The speed of high-carbon material—$0 \cdot 65$–$0 \cdot 85\%$ carbon content—is, in general, 30% less in diameters as stated. The following figures furnish average reduction speeds for various commencing diameters :

Size	$0 \cdot 80\%$ carbon	$0 \cdot 15\%$ carbon
1/0 S.W.G. (0·324)	104/110 ft./min.	150/250 ft./min.
3 S.W.G. (0·252)	150/200 ft./min.	250/300 ft./min.
5 S.W.G. (0·212)	250/300 ft./min.	300/450 ft./min.

The speed is increased as the material is reduced finer.

A one-draft machine, employed for heavy work such as reducing $\frac{9}{16}$ in. and $\frac{1}{2}$ in. dia. material to smaller sizes in one draft, is illustrated in Fig. 4. The bulk of bright hard drawn steel bars, in sizes from $\frac{9}{16}$–$\frac{1}{4}$ in., are processed on this type of machine, the material being produced in coil form, then transferred to a special machine for straightening and cutting into lengths. The one-draft type is also widely employed for the production of sectional units from cylindrical stock.

The most striking characteristic of cold-drawn carbon steels are their high tensile strength, tensile or breaking strain of steels commonly employed in the fabrication of colliery winding ropes varying from 100–130 tons/sq. in.

In the production of high-carbon steel wires, as employed in mining ropes, it is customary to subject the finished units to empirical torsion and flexion tests, as a means of determining ductility and uniformity. In torsion testing the wire is caused to twist under the influence of an axially applied couple, and number of twists to failure in 100 diameters is, in general, taken as a measure of the quality of material.

The torsion test is rarely employed in Continental specifications, producers maintaining this to be too severe, and tending to exclude material suitable for use in rope fabrication. The flexion test, rarely employed in Great Britain, is the standard for ductility on the Continent.

In flexion testing a straight piece of wire is held in a vice between two cylindrical rollers of specified radius, and caused to bend to and fro over rollers until fracture occurs. The number of bends to failure is taken as a measure of ductility, and the minimum number for the various diameters are prescribed in the specification.

Fig. 2.—A continuous machine for further drafting to 21 S.W.G.
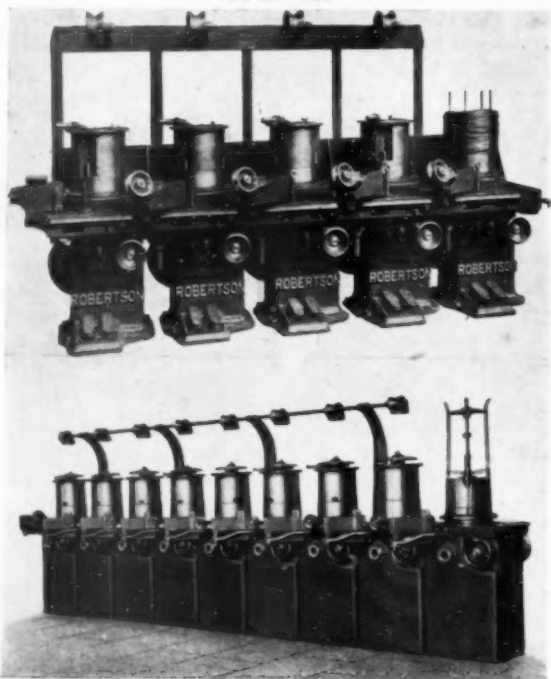
Fig. 3.—A nine-hole drafting machine for reducing the material to 30 S.W.G.

Where plastic deformation is carried to excess a point is eventually reached at which the material refuses further reduction ; fracturing immediately tensile stress is applied. In this condition it is termed " over-drawn," ductility being exhausted by too great a reduction in the cross section.

Over-drawn defects are easily identified by condition of the fracture when the material is subjected to tensile test, fractured ends revealing little, if any, contraction at the breaking point ; one side of the fracture furnishing a pointed cone, the other showing a corresponding conical depression.

This type of fracture is commonly known as " cuppy," and is easily distinguishable from the tensile fracture of ductile material, which furnishes a local reduction of cross-section at the point of failure, and a truncated conical fracture.
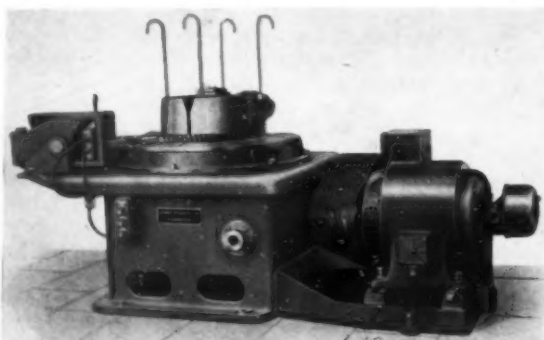
Fig. 4.—A one-draft machine for heavy work, such as the reduction of $\frac{9}{16}$ & $\frac{1}{2}$ in. dia. material to smaller sizes in one draft.

Correspondence

The Degassing of Bronzes by Oxidation Treatment

The Editor, METALLURGIA.

Dear Sir,

The views on the degassing of tin bronzes and phosphor-bronzes by oxidation treatment, expressed by Dr. Pell-Walpole in his article in METALLURGIA, January, 1948, call for comment, both on the observed facts and on the theories of gas-metal equilibrium which he invokes.

My colleagues and I have shown (*Jour. Inst. Metals*, 1941, 67, pp. 241, 242, 245, and Figs. 3A, 5 and 5A) that copper-tin alloys melted and cast in an atmosphere containing 89% N_2 and 11% H_2 gave chill castings apparently free from gas porosity but contained enough hydrogen to show marked gas unsoundness in sand castings. Typical results are set out below :—

Melting Atmosphere	Chill Cast*		Sand Cast*	
	Density g./cc.	Tensile Strength tons/sq. in.	Density g./cc.	Tensile Strength tons/sq. in.
Dry Nitrogen ..	8·88	13·9–23·8	8·82	19·3–20·5
89%N_2, 11%H_2	8·87	20·9–24·4	8·67	11–16

* Average density and range of tensile strength for bars chill cast at 1,050°-1,200° C. or sand cast at 1,050°-1,150° C.

Following the earlier recommendations of Genders and Bailey ("The Casting of Brass Ingots," B.N.F. M.R.A. Res. Monograph No. 3, 1934), the castings were poured as slowly as possible (1 in. dia. bars, pouring aperture in crucible $\frac{1}{8}$ in. in dia.) to minimise shrinkage porosity and the highest densities obtained approached the maximum density of the alloy (8·96 gm./cc. for the wrought homogenised alloy, and probably 8·92–8·93 gm./cc. for the duplex structure of "as-cast" material). Chill bars poured under pressure of 0·005 mm. mercury had a density of 8·87 gm./cc. and the small amounts of porosity in the chill and sand castings made in nitrogen atmospheres can therefore be safely ascribed to shrinkage. Melts made in 89/11 N_2/H_2 atmospheres gave sand castings with considerably increased unsoundness which must be due to gas, while chill castings from melts of the same gas content show no significant decrease in density. Thus the chill casting is insensitive to the effect of gas below a certain critical content.

It is also noteworthy that the mechanical properties of chill castings from the "gassy" melts had high strengths more consistently than those made from "gas-free" melts, an observation which was explained by the occurrence of localised patches of shrinkage porosity in the latter.

In later work on methods of degassing bronzes (*Journal of the Institute of Metals*, 1944, 70, 349) we therefore used sand castings rather than chill castings to detect gas remaining in bronze melts after degassing treatments. We found that copper-tin alloys, with or without initial phosphorus contents not exceeding about 0·05%, were rapidly degassed by treatment with oxidising fluxes. For example, melts gassed with hydrogen giving sand cast test bars with densities of about 8·55 gm./cc. yielded sand cast test bars with densities between 8·75 and 8·80 gm./cc. after oxidation with approximately 1% of a 50/50 CuO/KNO_3 flux for 5 minutes followed by deoxidation before pouring. On the other hand, bronzes containing 0·2 to 0·4% phosphorus, or more than about 0·5% zinc, were not degassed by similar treatment, but were easily degassed in five minutes by scavenging treatment with inert gases. In the same work we measured the oxygen contents of a number of copper-10% tin-phosphorus alloys after treatment with the oxidising flux. In the absence of phosphorus the oxygen content attained a maximum value of about 0·02%, while the presence of a residuum of 0·005% of phosphorus lowered the oxygen content to 0·004%. Higher phosphorus contents lowered the oxygen content even further, the lowest values found being of the order of 0·002% oxygen with 0·01% or more phosphorus. From these results and Allen's classical work on the molten copper/steam equilibrium, we concluded that the presence of phosphorus and zinc in tin bronzes retarded the oxidation of hydrogen and imposed a limit below which the hydrogen content could not be reduced by oxidation treatment in practice. We concluded from our results that the hydrogen content of alloys which after oxidation contained more than 0·5% zinc and/or any appreciable amount of phosphorus, could not be sufficiently lowered by oxidation to ensure freedom from gas porosity in sand-cast material, and that scavenging treatment with inert gases was much more effective.

In his recent article Dr. Pell-Walpole states that he has found oxidation treatment an effective method for degassing bronzes containing phosphorus and zinc and that his results differ from those obtained by us. He therefore suggests that our explanation of the mechanism involved in the process is all wrong. To deal with facts first, Dr. Pell-Walpole's conclusions are based entirely on the properties of chill castings, whereas ours are based upon the properties of sand castings, which, as the foregoing data shows, are much more sensitive to the effect of gas. I cannot agree therefore that Dr. Pell-Walpole's experimental facts are at variance with ours. We have already shown (*Jour. Inst. Metals*, 1944, 70, 587) that the flux, 1 CuO, 1 borax, 1 sand, described at that time by Dr. Pell-Walpole did not degas an 89·5/10/0·5 Cu/Sn/P alloy to an extent adequate to give sound sand castings. In these experiments, melts were "gassed" with hydrogen and poured into sand moulds dehydrated by baking at 900° C. to avoid gas absorption from the mould. The cast bars had densities of the order 8·5–8·6 gm./cc. Similar melts subsequently oxidised for 20 minutes with 2% by weight of the flux gave bars with densities of the order 8·5–8·7 gm./cc. The maximum density of this alloy is approximately 8·88 gm./cc., and sand-cast bars with densities of 8·75 to 8·80 gm./cc. were obtained consistently when the melt was scavenged with inert gas.

From the earlier discussion of the mechanism involved, it is however to be expected that oxidation would remove hydrogen in excess of a certain amount and further, the degassing effect of a given type of oxidising flux would increase as the oxygen content of the flux is raised, because the oxygen concentration in the molten metal would thereby be increased. I have therefore examined the effect of the 2 CuO, 1 borax, 1 sand flux described in Dr. Pell-Walpole's recent article, using it to treat an 89/10/1 Cu/Sn/P alloy. It will be remembered that from the properties of the chill cast material, Dr. Pell-Walpole concludes that this flux degasses this alloy adequately for practical purposes.

To allow direct comparison with Dr. Pell-Walpole's results, both chill castings 2 in. diameter, poured at 8 lbs./min. and sand-cast DTD bars (moulds baked at 800° C.) have been made, with the following results :—

Treatment of Melt	Density Gm./c.c.		
	Chill		Sand
(1) 50 lb. melt heated to 1,250°–1,300° C., " gassed " with H₂	8·403	..	8·44
(2) As (1), plus 5 minutes blowing with N₂	8·795	..	8·725
(3) As (1), plus 10 minutes oxidation with 3% of flux	8·794	..	8·63

The chill bars were cast at 1200° C. and for convenience the sand castings from the same melts were also poured at 1200° C., although this relatively high casting temperature of course increased the shrinkage voids in the sand-cast bars. The maximum density of the alloy is approximately 8·84 gm./cc.

The results speak for themselves, and illustrate once again that oxidation treatment may degas adequately to give sound chill castings but leave enough gas in phosphor-bronze melts to produce marked gas unsoundness in sand castings.

Dr. Pell-Walpole's results and our own are readily explained qualitatively by the generally accepted theory of gas-metal equilibria. The main reaction involved is :

$$2H + Cu_2O \rightleftharpoons 2Cu + H_2O$$

where the left hand side refers to components dissolved in the metal. Given an initially high hydrogen content the reaction will proceed rapidly to the right, with resultant removal of hydrogen from the melt, provided that the oxygen content of the melt is raised to a value such that the partial pressure of steam exceeds one atmosphere, in which case bubbles of steam are formed and escape from the bath. When the hydrogen content of the bath has fallen to a value such that :

$$\frac{(H)^2 \, (O)}{k_1} < 1,$$ (where (H) and (O) are the oxygen

and hydrogen concentrations in the bath respectively, and k_1 is an equilibrium constant) further steam evolution can only occur by evaporation from the surface of the bath and diffusion of the steam away from that surface. This latter process is too slow to allow of degasification in a reasonable time.

To avoid gas porosity in a casting, the residual hydrogen content of the metal must be lower than the amount which can be retained in solid solution, and this is evidently higher for chill castings than for sand castings. The amount of hydrogen which can be retained in solid solution cannot be calculated with sufficiently high precision to decide whether or not a given-oxygen content of the metal will give the desired result, because the amount of hydrogen producing say ·5% voids in a sand casting is only a fraction, about ¼th of the solid solubility calculated from existing data.

Nevertheless, the fundamental work by Allen is quite adequate to account for the observed facts in a qualitative way and I fail to see why Dr. Pell-Walpole should think it necessary to postulate a new theory, and particularly one which appears to be utterly inconsistent with the laws of physical chemistry.

Thus it appears that Dr. Pell-Walpole does not agree that the removal of hydrogen from the molten bronze is conditioned by the oxygen concentration in the melt and he postulates a reaction at the slag/metal interface which proceeds independently of the distribution of oxygen between the slag and the molten metal. Numerous examples could be cited of surface reactions which proceed to completion in one direction without regard to the concentrations of one or more of the reactants, but the controlling factor in such cases is the rapid removal of the reaction products from the reaction zone. Evidently, however, Dr. Pell-Walpole does not postulate such conditions in his new theory for the degasification of bronze by oxidation, for he states that the reaction product, steam, escapes from the slag/metal interface as bubbles. If steam bubbles are formed, and if the usual laws of physical chemistry are obeyed, the steam will be partially dissociated according to the equation (2) :

(2)
$$\frac{(pH_2)^2 \cdot (pO_2)}{(pH_2O)} = K_2$$

and thus the molten bronze is in contact with an atmosphere containing hydrogen. The hydrogen content of the metal will therefore tend to a value given by :

(3)   (H) in metal $= K_3\sqrt{(pH_2)}$

and when it falls to this value the evolution of steam will cease. The hydrogen concentration in the metal can only be lowered further by reducing (pH_2) in equations (3) and (2) which involves increasing (pO_2) in equation (2). This in turn involves an increase in the partial pressure of oxygen in the molten metal because :

(4)   (O) (in metal) $= K_4\sqrt{(pO_2)}$

I have done my best to develop Dr. Pell-Walpole's hypothesis to a logical conclusion but am driven back to the view I have previously expressed, namely that the degasification of molten bronze by oxidation treatment under practical foundry conditions, is controlled by the oxygen concentration in the melt. I am prepared to believe that oxidation treatment will reduce the hydrogen content to a level tolerable in sand castings, if and when I see evidence that such is the case. Dr. Pell-Walpole has not yet produced such evidence, and our own observations lead me to the conclusion that, although this treatment offers a useful method of reducing the hydrogen content to a limited value, this value is still too high for most types of sand castings.

Yours faithfully,

W. A. BAKER, *Senior Metallurgist*,
British Non-ferrous Metals Research Association.
Euston Street,
     London, N.W. 1.
March 3rd, 1948.

Reply from Dr. Pell-Walpole

The Editor, METALLURGIA.

Dear Sir,

Mr. Baker's contribution on the subject of degassing bronze is very welcome, and summarising, as it does, much of the excellent work of B.N.F.M.RA. on degassing for sand casting, is in large measure complementary to my own work which relates solely to chill casting.

With regard to differences of opinion as to the mechanism of degassing, the issue was perhaps rather clouded by the absence of a fuller discussion on this matter in the original article in an attempt to save space.

The fundamentally important reaction is, of course,

$$H_2 + Cu_2O \rightleftharpoons H_2O + Cu$$

It is established by the B.N.F.M.R.A. works that this reaction is reversible and that the residual hydrogen in solution in copper or in the low-phosphorus bronze depends on the oxygen content of the metal, on the pressure of steam in the atmosphere and on temperature.

The solubility of oxygen in bronze containing excess phosphorus however is known to be very low, and this oxygen content cannot be increased, unless the phosphorus is reduced to below 0.02%. Therefore, if the degassing of phosphorus bronzes depends solely on the oxygen dissolved in the metal as represented by Mr. Baker's equations $2-4$, then its progress should not vary with the oxygen content of the flux, since an increase of the latter cannot increase the oxygen content of the metal. The analytical results show that phosphorus content remains far above the limiting 0.02%. Mr. Baker is incorrect, therefore, in stating that the increased oxygen content of the flux will increase the oxygen content of the metal. It is shown in the paper, however, that the degree of degassing does increase, i.e., the residual hydrogen content decreases as the oxygen content of the flux increases. My explanation of this is that the oxygen in the flux can react at the flux metal interface directly with the hydrogen of the metal, the oxygen content of the latter remaining constant, being conditioned by the persisting high phosphorus content of the metal. The source of the oxygen in the degassing reaction, is the only difference which I propose from the generally accepted mechanism, in order to account for the beneficial effect of increasing the available oxygen content of the flux. The reaction from which should be written—

$$O \text{ (in flux)} + 2H \text{ (in metal)} \rightleftharpoons H_2O. \quad (A).$$
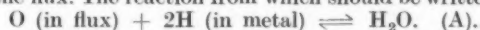
Since the steam formed can escape from the system as bubbles, the reaction will proceed from left to right, but the time factor is important since the hydrogen in the metal and the oxygen in the flux must diffuse to the reaction surface, i.e., the flux/metal interface. Therefore the time which molten metal and molten flux are in contact should be of importance in determining the extent to which degassing proceeds. The author has obtained the best results when the flux is charged with the metal, a procedure which gives maximum time of contact between flux and metal.

The flux/metal reaction will reach a state of equilibrium when the pressure of steam generated is less than 1 atmosphere so that the steam can no longer escape from the system by bubbling through the flux. The equilibrium of the system may then be represented by the equation—

$$\frac{[O]\ [H]^2}{P.H_2O} = K. \quad (B).$$

Where O is the concentration of available oxygen in the flux.

H is the concentration of hydrogen in the metal.

K is the equilibrium constant.

P.H$_2$O the pressure of water vapour.

The essential difference between equation B and Mr. Baker's equation (2) is that the oxygen is the concentration in the flux in equation B and the concentration in the metal in Mr. Baker's equation (2).

It follows from equation (B) that the higher the oxygen concentration in the flux (i.e., the higher its CuO content) the lower is the residual hydrogen content of the metal which is in accordance with the experimental results reported in the original article.

As to whether the residual hydrogen content is low enough to be harmless enough for the process to be beneficial in practice depends on the type of casting being made, with special reference to—

(1) the rate of cooling of the casting.

(2) the possibility of hydrogen being absorbed during the casting process by reaction with sand or similar material containing combined water.

With regard to (1), as Mr. Baker rightly contends, a chill casting can retain much more hydrogen in super-saturated solid solution than can a slowly cooled sand-casting, so that a residual hydrogen content, which proves to be quite harmless in a chill-casting, may cause objectionable porosity in a sand casting. My own work related solely to chill castings, in which it is shown that sensible freedom from gas porosity can be secured by using a flux of high CuO content, even when gassy charges are to be handled.

These conclusions clearly must not be applied to sand casting unless evidence is produced that the residual hydrogen content is not sufficient to cause appreciable porosity with the lower cooling rate involved. The chief difficulty in establishing the case for sand casting is that the metal absorbs hydrogen from the mould, but I am at present engaged in research on this subject, and the results will be published later. Meanwhile Mr. Baker has kindly supplied some test results obtained when using a high oxygen content flux with a gassy charge of a phosphorus bronze. These confirm that a chill casting produced by this process is virtually free from gas porosity, with a density equal to that given by the nitrogen scavenging process. With a casting made in a sand mould baked at 800° C. which eliminates factor (2) above, the flux when applied only for ten minutes, instead of for the whole melting time as in my recommendations gives only partial degassing, the residual hydrogen content being sufficient to cause an appreciably lower density as compared with that obtained by the scavenging process. Although this appears to be the result of only a single test series we may assume that it was carried out under strictly comparative conditions and that subject to the limitation noted above with regard to time of application of the flux, it establishes that the flux process does not remove hydrogen so completely as the nitrogen process. This, in any case, would not be disputed on theoretical grounds.

The fact remains however, that in normal sand-casting practice factor (2) is very important. Moulds are not dehydrated by baking at 800° C. and could not be so treated. In consequence, therefore, a sand-casting in phosphorus-bronze does absorb hydrogen from the sand mould. This fact is well established by works published by B.N.F.M.R.A. and by the Tin Research Institute. It seems likely, therefore, that no special merit can be attached to the complete removal of hydrogen during melting, and that a process which removes all but the last traces would be equally beneficial in practice. Quantitative data on this subject must await the results of further researches which are at present in progress but many foundries have already satisfied themselves as to the usefulness of the flux degassing process.

Yours sincerely,

W. T. PELL-WALPOLE.

Metallurgy Dept., The University,

   Birmingham, 15.

March 23rd, 1948.

Metals and Mankind

The Editor, METALLURGIA.

Dear Sir,

   Table I of my lecture published in your issue for March gives analyses of ancient British and Roman irons. Mr.

M. M. Hallett has very kindly pointed out a misprint in one of the sources from which I obtained information. The slave gang chain was reported to contain 1·05% phosphorus, but Sir Cyril Fox states that two figures became transposed in the Cardiff Report, and the value should be 0·15%. The Roman chisel in the same Table had a carbon content ranging from 0 to 1·3%.

Yours faithfully,

HUGH O'NEILL.

University College,
Swansea.
31st March, 1948.

Free Cutting Stainless Steel Castings

In recent years, aircraft engine developments have demanded steels of a similar type to the corrosion-resisting category for use at high temperatures, and for reasons of design the components have been produced in the cast, rather than the wrought, form. Production engineers are familiar with the machine shop problems, due to the inherent characteristics of these steels, particularly the austenitic corrosion-resistant types. The problems have been somewhat mitigated by the development and application of special machining techniques which has shortened the time taken in machining operations, but there are limits to the improvement which is possible by these means. A substantial contribution towards solving the problem, however, has been based upon a metallurgical modification involving the addition to these classes of steel of small proportions of special elements, which in principle follows the measures taken to improve the machinability of the straight carbon and low alloy steels.

The complexity of the machining operations involved in many aircraft engine castings led to the application by The David Brown Foundries Company of those measures which had previously proved successful in improving the machining characteristics of the wrought corrosion-resisting steels, and arising from this, it has been possible to extend such free-cutting characteristics to the well-known types of stainless and corrosion-resisting steels produced as castings. This object has been achieved without reducing to any marked extent the mechanical and other special properties associated with such materials. Emphasis is laid upon the difficulties of defining precisely the extent to which machinability has been improved, on account of the many well-known variables which make the assessment of machinability so complex. Experience, however, has shown that improvement is considerable, but it is suggested that this can be best ascertained for particular operating conditions by trial of cast material, which is available in the following types of steel—viz., 13% chromium; 18% chromium, 8% nickel; 18% chromium, 8% nickel, 1% columbium (weldable); 18% chromium, 8% nickel, 1% columbium, 3% molybdenum (weldable); 25% chromium, 12% nickel, 3% tungsten.

This David Brown development is felt to be of considerable importance in relation to present-day circumstances under which both man-power and machine capacity are at such a premium, and production engineers familiar with the machine shop problems presented by highly alloyed steel castings will welcome the advent of the free-cutting stainless and corrosion-resisting steel casting.

Steel Production in Germany

THE problem of the future steel production and the many difficulties involved formed the background to the recent general meeting of Verein Deutscher Eisenhüttenleute. Such difficulties as shortage of coal, energy and labour, the uncertainty as to what works will be kept going in the future, and other unsolved problems were discussed on a strictly professional basis, in contrast to former metallurgical conferences. At this meeting, the first since Germany's collapse, members as well as the public were made aware of the tasks facing the German iron and steel industry. At the same time efforts were made to explain the conditions to be fulfilled in order to accomplish these tasks.

The meetings of the " Verein " were always popular, but it is almost impossible to overestimate the interest taken in this meeting. Originally it was planned to be held in the Opera House, but the response by members to invitations to attend the meeting were so great that it had to be transferred to the Europa Palast Theatre. Even so, it was impossible to cope with the enormous flow of visitors, since about 2,000 members had accepted the invitation.

At the outset the meeting decided upon the new constitution of the Verein and the special committees. Dr. Ing. E. Herzog, chairman of the Board of Management of August-Thyssen-Hütte A.G., presided. Following elections and a financial statement, Dipl. Ing. K. P. Harten dealt in detail within the framework of a report on the activity of the Verein. He reported that a satisfactory start had been made by most of the special committees. Then he referred briefly to the collaboration between authorities and consumers in order to draw attention to vital needs.

Several papers were presented dealing with vital tasks and problems. The subjects discussed included interdependence of blast-furnace burden and fuel economy in iron and steel works; blast-furnace slags for reconstruction work; the iron industry and farm produce; the importance of high-grade steel for reconstruction work; and the development of rolled steel as to demand and manufacturing programme. All these papers, it will be noted, were concerned with present shortages, the ore problem taking precedence in importance.

The first paper showed that for smelting more heat is consumed when charging a poor burden and that the dressing of poor ores requires considerably more heat. On the whole a burden poor in iron will have a very adverse effect on fuel economy. The next discussed blast-furnace slags, the value of which has been raised through treatment and working at the iron and steel works. The use of blast-furnace slags it was stated should help to improve the German raw material position. The third paper surveyed the fertiliser position of German agriculture. The iron industry and the production of fertilisers are linked up in a double way by the use of slags for fertilisers on the one hand and the procurement of iron for the fertiliser industry on the other. The fourth paper which was supported by data, emphasised the need for larger quantities of alloyed steel. The last paper dealt with the carefully planned use of rolled steels emphasising, for instance, that the production of wide strip involves considerable savings in raw materials, heat, mechanical energy and, especially, labour. It, therefore, follows that such plants in Germany are vital.

Phosphate Treatments for Zinc Surfaces

By E. E. Halls

The rapid expansion in the use of zinc has emphasised difficulties encountered in securing the adhesion of organic coatings to this material and the possibilities of phosphate treatments, so successful for iron and steel, have been investigated. A number of phosphate treatments for zinc have been developed and test results are given in relation to some of these treatments applied to zinc in various forms.

PHOSPHATE processes have been established as a link in the production of rust-proof coatings for iron and steel, whether the latter be in the form of raw material or components. Properly designed processes applied under controlled conditions enable iron and steel to be rust-proofed with organic coatings of oil, wax, paint, varnish or enamel and the phosphate treatment performs several functions. It gives a coating by converting the surface layers of metal to a complex phosphate intimately bonded to the base material. This provides a key for the organic coating, because it is porous and granular so that good adhesion is assured. In a manner not clearly understood it retards the natural deterioration of the organic film so that ageing by softening or by embrittlement is very much delayed. In conjunction with the organic film is produced a rust-proof finish, insofar as rusting does not occur through the organic films and if the organic layer is scratched, chipped or otherwise rendered discontinuous then rusting is likewise localised at the rupture. The extent of this rusting is not so great as it would be in the absence of the phosphate coating and the latter prevents the spread of the rust beneath the organic film.

The rapid expansion in the use of zinc, particularly in the form of die-castings, as well as zinc coatings, such as electro-plate spray, or hot-dipped coverings for iron and steel and other metals, has brought very much to the fore difficulties that are encountered in the organic coating of zinc in these forms. The organic coating may be paint, varnish, enamel or lacquer and it may be required for appearance reasons or it may be necessary to retard the deterioration of the zinc itself by corrosive influences.

Zinc has always been notoriously difficult to paint, it being difficult to provide adhesion and when adhesion has been provided, it has been lost after a short period of service, due probably to the reaction between the zinc and constituents in the organic coating. A number of procedures have been adopted to overcome this shortcoming. The most satisfactory is probably the natural weathering given to galvanised iron structural work prior to painting, the paint adhering better to the weathered surface. This, of course, is too uncontrollable a process for industrial usage and the results from it are also variable.

Other treatments have been used, such as swabbing with solutions of copper salts, but without any real degree of success. The fact that phosphate processes are used satisfactorily for iron and steel work in a variety of forms makes it attractive proposition to use the same processes or similar processes for zinc base materials, providing, of course, they can be adapted to give successful results.

The position to-day is that a number of phosphate treatments have been developed for zinc and a number of those that are used for iron and steel are also used. This is satisfactory, with the reservation that at the moment it cannot be said that maximum efficiency can be obtained from any single process in all circumstances. This fact will be examined below on the basis of test results in relation to a number of phosphate treatments as applied to zinc in a variety of forms.

Test results are presented for organic enamel finishes on die cast zinc components, on electro-plated zinc steel components, on galvanised steel sheet and on zinc sprayed steel sheet. The specimens examined included those with and without phosphate treatment and in some cases included treated zinc without organic finish. The test conditions to which specimens were subjected comprised the following :—

(*a*) *Fluctuating conditions of warmth and humidity.*— In this test the samples were subjected to an atmosphere of 55°–60° C. during the 8-hour day, with a humidity of 65–75%, cooling off at night to atmospheric temperature, with a rise of humidity to 100% and condensation of moisture upon the specimens.

(*b*) *Open Atmospheric Exposure.*—Under these conditions the specimens were exposed from a rack facing south-west in open weather conditions of a semi-industrial atmosphere, without any protection from direct rain, wind, dirt, etc.

(*c*) *Salt Spray.*—One of the standard forms of test was employed, in which the samples were subjected to the mist produced by atomising 20% salt solution with compressed air. The atomiser was operated during the 8-hour day and the specimens left in the mist-laden cabinet for the remainder of the period. They were removed, washed in cold flowing water and dried on a soft cloth at the commencement of each day.

In the periodic examination of the specimens, attention was given to the extent of deterioration of the enamel finish and this was assessed by appearance, by scratch and bend tests. Results have been very briefly summarised in tabular form. The type of phosphatising process covered by the tests, included those specially marketed for zinc castings and those commonly used for steel work. All these require the work to be clean, i.e., thoroughly degreased and free from any corrosion products before treatment. Phosphate processes A and E represent two specifically intended for zinc castings and they are immersion processes using proprietary

Sample No.	Organic Finish	Without Chemical Pretreatment	Phosphatised by Immersion by Method :				Chemically Treated by Chromate Process
			A	D	E	F	
1	A	Adhesion poor in 7 weeks.	Unaffected in 104 weeks.	Unaffected in 52 weeks.	Unaffected in 104 weeks.	Unaffected in 52 weeks.	Unaffected in 104 weeks.
2	B	Enamel brittle and easily flaked in 3 weeks.	Only slight embrittlement of enamel in 104 weeks, adhesion still good.	Enamel embrittled and adhesion rather poor in 12 weeks.	Only slight embrittlement and very little depreciation in adhesion in 104 weeks.	Enamel embrittled with loss of adhesion in 12 weeks.	Only slight embrittlement of enamel and little loss of adhesion in 104 weeks.
3	C	Satisfactory in 12 weeks and reasonably good in 52 weeks.	Whitish in 30 weeks, lacquer too thin for full protection.	Unaffected in 52 weeks.	Whitish in 30 weeks due to lacquer being too thin for full protection.	Unaffected in 52 weeks.	Unaffected in 104 weeks.
4	D	Enamel soft and blistered, and could be peeled off in 3 weeks.	Unaffected in 104 weeks.	Unaffected in 52 weeks.	Unaffected in 104 weeks.	Unaffected in 52 weeks.	Unaffected in 104 weeks.
5	E	ditto	ditto	ditto	ditto	ditto	ditto
6	F	ditto	ditto	Slight embrittlement of enamel and a little loss of adhesion in 30 weeks, little further change in 60 weeks.	ditto	Slight embrittlement and a little loss of adhesion in 30 weeks little further change in 60 weeks.	ditto
7	G	ditto	ditto	ditto	ditto	ditto	ditto
8	H	ditto	ditto	ditto	ditto	ditto	ditto
9	I	ditto	ditto	ditto	ditto	ditto	ditto

Sample No.	Organic Finish	Without Chemical Pretreatment	Phosphatised by Immersion by Method				Chemically Treated by Chromate Process
			A	D	E	F	
1	A	Adhesion poor in 4 weeks.	Unaffected in 8 weeks.	Unaffected in 8 weeks.	Unaffected in 8 weeks.	Unaffected in 8 weeks.	Unaffected in 8 weeks.
2	B	Adhesion nil in 4 weeks.	ditto	Very slight embrittlement of enamel in 8 weeks, but adhesion still very good.	Enamel very slightly embrittled in 8 weeks, but condition still very good.	ditto	ditto
3	C	Unaffected in 8 weeks.	Very slight white corrosion in 8 weeks.	Unaffected in 8 weeks.	Unaffected in 8 weeks.	Very slight white corrosion in 8 weeks.	ditto
4	D	Adhesion very poor in 4 weeks.	Unaffected in 8 weeks.	ditto	ditto	ditto	ditto
5	E	ditto	ditto	ditto	ditto	ditto	ditto
6	F	Adhesion nil in 4 weeks.					
7	G	ditto	ditto	ditto	ditto	ditto	ditto
8	H	ditto	ditto	ditto	ditto	ditto	ditto
9	I	ditto	ditto	ditto	ditto	ditto	ditto

chemicals operated short of boiling, with an immersion period of 10–15 minutes.

After treatment, the work is thoroughly washed in water and dried. Processes of this nature are very active and produce a degree of transformation of the zinc surface to phosphate that is readily visible. They are, perhaps, the best processes for the phosphate treatment of solid zinc or zinc alloys. They may be too re-active for certain types of zinc coating.

Processes B, C and F are normal phosphate treatments for steel work. Of these, C is one of the nitrate accelerated types of solution which is very quick operating, so that treatment can be obtained in about 3 mins. using a temperature of about 186° F.

Process D is a similar one in which the solution is applied by spray instead of by immersion, with a treatment time of about one minute.

Before examining the value of these phosphate pretreatments on applied zinc coatings, it is useful to evaluate their usefulness on solid zinc such as zinc base die-castings.

Tables I–IV are presented for this purpose. They are mainly self-explanatory.

Table I refers to performance of enamelled zinc castings under the humidity conditions. Without any chemical pre-treatment, with the exception of Sample No. 3, having a special lacquer finish, it will be seen that all the finishes very quickly fail due to softening or embrittlement and loss of adhesion in a few weeks. With phosphate treatment, all of the finishes are very good and those combined with the longer phosphate immersion treatments, A and E are exceptionally good.

For comparison, results for a special chromate chemical treatment are included. Actually, the performance of the finishes including this treatment, are the best of the whole series.

The chromate treatment involved is a chemical immersion process applied to cleaned work, the method of cleaning not being very important, providing it produces grease-free surfaces. Actually, the samples concerned were electrolytically cleaned for 10–20 secs. in a solution of 8 ozs. of tri-sodium phosphate per gallon and then thoroughly water washed. For parts that are corroded, this alkaline clean can be preceded by an immersion treatment for 1–2 mins. in a solution of 30 ozs. of chronic acid/gallon, operated short of boiling. The wet work from the cleaning is then chromated in a solution of 34 ozs. of sodium dichromate crystals and 3 ozs. of sulphuric acid/gallon of water. This is worked at ordinary temperatures of 18°–25° C. and the immersion time is from 5–15 secs. After treatment the work is washed in cold water until no chromate is perceptible in the water draining off the parts and then dried at ordinary temperatures, if preferred, in a current of air at atmospheric temperature.

The chromated parts are allowed to age by exposure over-night before enamelling. This treatment is very similar to the chromate passivation treatment generally used for zinc, such as that covered by DTD. Specn. No. 923. It differs, in that the solution is a little more acid and that subsequent washing and drying must be performed cold. It is considered that these two modifications are beneficial in yielding an improved passivated film.

Sample No.	Organic Finish	Without Chemical Pretreatment	Phosphatised by Immersion by Method: A	D	E	F	Chemically Treated by Chromate Process
1	A	Adhesion very poor in 4 weeks; white corrosion from edges and holes.	Slight corrosion from edges and holes in 3 weeks, but enamel adhesion still good in 4 weeks.	Slight corrosion from corners in 3 weeks, but otherwise quite sound in 4 weeks.	A little corrosion from corners in 3 weeks, but otherwise quite sound in 4 weeks.	Slight white corrosion at edges and holes, and slight loss of adhesion near edges in 4 weeks.	Unchanged in 4 weeks.
2	B	Enamel blistered and easily peeled off in 3 weeks.	ditto	Cellulose enamel more brittle, but adhesion still reasonable in 4 weeks.	ditto	Cellulose enamel embrittled and tending to flake in 4 weeks.	Cellulose enamel slightly embrittled but adhesion still good in 4 weeks. No corrosion.
3	C	Very little deterioration in 4 weeks.	Light corrosion general in 4 weeks.	Very slight general corrosion in 4 weeks.	Slight general corrosion in 4 weeks.	Very slight general corrosion in 4 weeks.	Unchanged in 4 weeks.
4	D	Finish softened and adhesion poor in 4 weeks.	Corrosion from edges and holes in 3 weeks. Enamel adhesion unaffected in 4 weeks.	Slight corrosion from edges, slight softening of enamel and a little loss of adhesion in 4 weeks.	A little corrosion from corners in 3 weeks, but otherwise quite sound in 4 weeks.	Slight corrosion and a little softening of enamel in 4 weeks.	ditto
5	E	ditto	ditto	ditto	ditto	ditto	ditto
6	F	Enamel blistered and easily peeled away in 3 weeks.	ditto	Slight corrosion at edges and very slight embrittlement of finish in 4 weeks. Condition still very good.	ditto	Slight white corrosion and slight embrittlement of enamel in 4 weeks.	ditto
7	G	Enamel blistered and easily peeled away in 3 weeks.	Corrosion from edges and holes in 3 weeks. Enamel adhesion unaffected in 4 weeks.	Slight corrosion at edges and very slight embrittlement of finish in 4 weeks. Condition still very good.	A little corrosion from corners in 3 weeks, but otherwise quite sound in 4 weeks.	Slight white corrosion and slight embrittlement of enamel in 4 weeks.	Unchanged in 4 weeks.
8	H	ditto	ditto	ditto	ditto	ditto	ditto
9	I	Much corrosion and adhesion very poor in 3 weeks.	Slight corrosion from edges, but enamel otherwise unimpaired in 4 weeks.	ditto	Slight corrosion from edges, but enamel unimpaired in 4 weeks.	ditto	ditto

TABLE IV.—FINISHES USED ON SPECIMENS IN TABLE Nos. 1-3

Finish No.	Composition of Finish
A	Single coat of aluminium cellulose lacquer.
B	Two coats of glossy pigmented cellulose enamel.
C	One thin coat of special cellulose lacquer.
D	Single coat of aluminium stoving enamel.
E	One coat of aluminium stoving enamel, and one coat of stoving varnish.
F	Two coats of glossy pigmented stoved enamel.
G	Red oxide primer and one coat of glossy finishing enamel.
H	Zinc chromate primer and one coat of glossy finishing enamel.
I	Two coats of synthetic lowbake matt black enamel.

Results of the open atmosphere test in Table II confirm those of the humidity test. The same applies to the results of the salt spray tests in Table III. The finishing schemes for the specimens covered by these Tables are briefly summarised in Table IV. It should be noted that Finish C which gives the best performance when no chemical pre-treatment is used, comprises a special nitro-cellulose-glyptal combination lacquer of low viscosity. It should also be noted that the best of the other finishes are the stoving aluminium enamel combinations of D and E. The actual characteristics of the finishing media used are given in Table V.

For zinc coatings, particularly if they tend to be thin, or thin and of irregular thickness, as is expected from electro-plated coatings, the more active phosphate processes such as A and E may be too re-active to be entirely satisfactory. This can be examined in the test results in Tables VII-X.

Table VI briefly summarises the behaviour of zinc die castings with and without the chemical treatment but with no organic finish when submitted to the various exposure tests. It will be seen that the heavier phosphate processes A and E tend to promote the development of white corrosion upon exposure. This is not nearly so marked with the less active phosphate processes D and F. The chromate immersion treated specimens withstood all the tests without any deterioration whatsoever.

Table VII gives some similar results on electro-zinc plated steel components. The tests embrace fluctuating humidity and the dry and wet cycles of WT. Board Specn. No. K.110. It will be seen that the mild phosphate treatment is very beneficial, showing up exceedingly favourable under both tests.

Table VIII refers to similar samples, enamelled, under salt spray and atmospheric exposure conditions. These specimens, it will be noted, were given the heavier phosphate treatment and the additional durability imparted thereby is very noticeable. The black enamel finish concerned comprised one coat of a bitumenised black stoving undercoat and one coat of a semi-gloss black finishing enamel, each coat being stoved for 2 hours at 150° C.

Table IX, again deals with similar samples and gives a comparison between organic finishes consisting

TABLE V.—LABORATORY CHARACTERISTICS OF ORGANIC FINISHING MEDIA REFERRED TO IN TABLE IV.

Finish No.	Description	Type	Chemical Characteristics		Physical Characteristics		Stoving Conditions
			Volatile Spirit %	Total Solids %	Specific Gravity at 25° C.	Viscosity Centipoises at 25° C.	
A	Aluminium cellulose lacquer.	Ready mixed.	92·5	7·5	0·839	85	—
B	Grey cellulose enamel.	Ready for spray, glossy.	66·0	34·0	1·010	600	—
C	Special cellulose lacquer.	Cellulose/glyptal product	88·0	12·0	0·880	12·5	—
D	Aluminium stoving enamel.	Ready mixed, oil modified glyptal type.	61·5	38·5	0·995	40	½ hour at 250° F.
E	Stoving varnish.	Oil modified glyptal type.	56·5	43·5	0·968	135	ditto
F	Grey stoving enamel.	Alkyd-urea synthetic.	62·3	37·7	1·038	380	ditto
G	Red oxide primer.	Oil modified glyptal type.	43·6	56·4	0·910	580	ditto
H	Zinc chromate primer	ditto	55·5	44·5	1·050	290	ditto
I	Lowbake black stoving enamel.	Urea base synthetic.	42·5	57·5	1·160	500	ditto

Sample No.	Chemical Treatment	Durability Under Test Conditions Comprising :		
		Salt Spray	Humidity	Open Atmosphere
1	None	White corrosion within a week, developing gradually to fairly heavy in 4 weeks.	Unaffected in 4 weeks, and with only a few isolated white corrosion spots in 30 weeks.	A few only isolated white corrosion spots in 4 weeks, very little worse in 30 weeks.
2	Phos Method A. Fairly heavy corrosion in 4 weeks.		Gradual slight whitening, fairly poor condition in 30 weeks.	White corrosion spots in 4 weeks relatively pitted in 30 weeks.
3	Phosphate Method D. Slight white corrosion in 4 weeks.		Unaffected in 4 weeks and only a few white corrosion spots in 30 weeks.	Slight corrosion in 4 weeks and little only further deterioration in 30 weeks.
4	Phosphate Method E. Fairly marked corrosion in 4 weeks		Gradual slight whitening developing to a rather poor condition in 30 weeks.	White corrosion spots in 4 weeks, developing to a pitted condition in 30 weeks.
5	Phosphate Method F. Slight white corrosion in 4 weeks.		Unaffected in 4 weeks and only a few white corrosion spots in 30 weeks.	Slight corrosion in 4 weeks and a little further deterioration in 30 weeks.
6	Chromate Immersion. Unaffected in 4 weeks.		Unaffected in 30 weeks.	Virtually no deterioration in 30 weeks.

Sample No.	Phosphate Treatment	Test Conditions	Period of Test	Behaviour under Test Conditions	
				Without Phosphate Treatment	With Phosphate Treatment
1 (a)	C	Humidity.	42 days	General staining of all surfaces.	Unaffected.
			300 days	General staining increased, some white corrosion, appearance rather dirty.	Unaffected.
1 (b)	C	WT Board Spec. K.110, 1 dry and 2 wet cycles.	3 days	Heavy white corrosion.	Unaffected.
		21 wet cycles.	22 days	Very heavy white corrosion, little rusting.	Slight very light white corrosion.

Sample No.	Phosphate Treatment	Test Conditions	Period of Test	Behaviour under Test Conditions	
				Without Phosphate Treatment	With Phosphate Treatment
1 (a)	A	Salt Spray.	21 days	Some rusting evident, enamel badly blistered and adhesion very poor.	Some rusting evident, a little blistering only, adhesion reasonably good.
1 (b)	A	Atmospheric Exposure.	21 days	Enamel coating very brittle.	Virtually unaffected, no embrittlement of the enamel, adhesion still very good.
2	A	None (condition as finished).		Enamel brittle and non-adherent on scratch test, and flaked on bending.	Enamel gave a clean cut on scratch test and showed good adhesion. On bend test enamel showed good adhesion to zinc.

of pigmented cellulose enamel and stoved synthetic enamel. Appreciable improvement in performance of the cellulose enamel finish results from the phosphate treatment and very marked improvement in the case of the stoving finish.

The results in Table X refer to similar zinc finishes, the phosphatising in this case being done by Method D. Comparing these results with those in the previous Table, it is seen that even this rapid light treatment of the zinc is very effective, although not so good as obtained by the immersion treatments.

Tables XI and XII appertain to galvanised steel. Enamel finishes in cellulose and stoved synthetic and air drying synthetic, are examined on this material, with and without the phosphate treatment. Method C was employed, but for a range of immersion times. The humidity test results in Table XI all show the same benefits imparted by the phosphate treatment as with the previous forms of zinc, i.e., much less ageing of the enamel at the end of the test and much superior adhesion on the samples where the phosphate treatment had been applied. The trend of results in Table XII with the samples under open atmospheric conditions is again the same, i.e., all finishes without phosphate treatment are unreliable and rapidly age and become non-adherent, whereas those with the phosphate treatment are quite serviceable.

Tables XIII and XIV deal with the same three finishes on steel panels, finished by means of zinc spray, using the wire process. Humidity and atmospheric test results agree in indicating the same thing, viz.,

that the finishes withstand these test conditions equally well whether phosphatising is applied or not.

These are surprising results and are fully borne out by experience in practice over many years. It is partly accounted for by the open structure of the surface of the zinc sprayed coating which provides an excellent key to ensure good adhesion of the enamel finish.

This cannot, however, be the whole explanation and it is probable that the slight oxidising of the surface of the zinc particules as they are sprayed on to the metal may have some bearing on the re-action between the zinc and the constituents in the paint film. In this case, there is some inhibiting effect, and the re-action must be negligible, otherwise adhesion would be lost in the same way as it is with enamel coatings on other zinc surfaces.

The air drying finishing media referred to in Tables XI–XIV are characterised in Table XV. The other media concerned are the same as those referred to in Table V.

The tabulated results presented are not by any means exhaustive, nor are they sufficient to give a full comparison of the various methods of chemical pre-treatment nor of their full advantages or disadvantages. They are, however, comprehensive in being a broad collection of practical data and it is significant that, with the exception of zinc sprayed surfaces, the phosphate treatments provide benefit in every case. It is evident from the results that further development work on the phosphate type of solution is necessary in order to arrive at the best treatment for each condition of the

TABLE IX.—DURABILITY TEST RESULTS ON ENAMELLED ZINC-PLATED STEEL COMPONENTS, WITH AND WITHOUT PHOSPHATE TREATMENT OF THE ZINC-COATED SURFACES

Sample No.	Phosphate Treatment	Test Conditions	Period of Test	Enamel Finish	Performance under Test	
					With Phosphate Treatment	Without Phosphate Treatment
1 (a)	B	Salt Spray.	7 days	Pigmented Cellulose (2 coats)	Slight blistering of enamel at edges.	Enamel cracking and peeling, corrosion of zinc coating : condition very poor.
			28 days		Deterioration spreading from edges, adhesion of enamel poor at edges.	
			42 days		Penetration of attack from edges to a depth of 1 in., but general surfaces still showing excellent adhesion.	
			90 days		Blistering fairly general and white patches appeared where zinc had corroded through the finish. Appearance poor, quality moderate.	
2 (a)	B	Salt Spray.	4 days	Stoved primer an stoved finishing enamel	Unaffected.	Enamel generally blistered.
			30 days		Slight blistering of enamel evident at edges, but adhesion of enamel still very good.	Enamel condition very poor, zinc corroding heavily.
			60 days		Slight blistering and deteriorated adhesion near edges. General adhesion good and appearance of main surfaces good.	Heavy general rusting.
			90 days		Blistering still confined to edges and areas within 1 in. of edges. General finish still very good.	
1 (b)	B	Humidity	14 days	Pigmented Cellulose (2 Coats)	Virtually unaffected, adhesion good.	Enamel very brittle on scratch test and non-adherent on bend test.
			42 days		Virtually unaffected, adhesion good.	
			112 days		Enamel brittle to scratch test and only showed moderate adhesion on bending. Finish classed as moderate.	
2 (b)	B	Humidity	42 days	Stoved Primer and Stoved finishing enamel	Virtually unaffected, adhesion good.	Enamel brittle on scratch test and rather poor on bend test, flaking rather easily at the bend.
			112 days		Enamel finish still showed no embrittlement on scratch test. On bend test, enamel cracked and could be flaked off the bend only with difficulty. Finish classed as good.	

TABLE X.—DURABILITY TEST RESULTS ON COMPONENTS, ELECTRO-ZINC PLATED, WITH PHOSPHATISING AND ENAMELLED

Sample No.	Phosphate Treatment	Test Conditions	Period of Test	Enamel Finish	Behaviour under Test Conditions	
					Zinc plating lightly wiped with steel wool before phosphatising	Phosphatised without wiping
—	D	Appearance	—	—	Light grey, texture of zinc unaffected by phosphatising.	Mottled light grey, texture of zinc unaffected by phosphatising.
1 (a)	D	Humidity	60 days	Cellulose enamel (2 coats)	Enamel very brittle on scratch test, and its adhesion poor on bend test.	Enamel very brittle on scratch test, and its adhesion very poor on bend test.
1 (b)	D	Salt spray	14 days	do.	Enamel film became whitish and blistered near edges.	Enamel film became dull and whitish, and blistered from edges.
			70 days		Corrosion of zinc through the enamel film. Enamel film brittle on scratch test and non-adherent on bend test.	Corrosion of the zinc through the enamel film, which had become very brittle on scratch test, and non-adherent on bend test.
1 (c)	D	Humidity	70 days	Stoved primer and stoved finishing enamel	Finish very brittle on scratch test and adhesion exceedingly poor on on bend test.	Finish a little brittle on scratch test and showed poor adhesion on bend test.

zinc. It is also evident that the chromate treatment cannot be neglected in such a study, but the reason that they have not figured more generally in the matter presented is that, with the one exception of the particular chromate immersion process cited, it is generally found that chromate passivation does not assist the enamel finish either materially or to the same degree as does the phosphate treatment.

One outstanding merit of these established phosphate processes is simplicity of control by elementary analytical methods applied at infrequent periods. This feature is so important that it cannot be over-emphasised. The new patents due to the Westinghouse Electric Corporation* are regarded as of importance from the point of view of a further and better understanding of existing processes, with special reference to zinc coatings, rather than from the angle of new and competitive processes.

U.S.P. No. 2310239 and B.P. Nos. 560847/8, are of especial interest in relation to the inclusion of a trace of titanium compound in the alkaline pre-cleaning solution. The origin of this was referred to earlier by F. J. Van Antwerpen.† The Westinghouse technicians had found that a preliminary rinse in a solution of disodium phosphate rendered the phosphatising of zinc plate really successful. The results could not be repeated however, until research by analytical and spectrographic methods revealed that the original disodium phosphate contained traces of titanium. The sodium diphosphate solution used is only 1% concentration and the salt contains only 0·001% of titanium. Immersion is at ordinary temperature for a period of only 10 secs. The zinc plated work is then passed on to an ordinary commercial phosphate process, and then for enamelling or painting, etc. The procedure is said to improve the

* *Metallurgia*, Oct., 1946, p. 320.

† *Chemical and Engineering News*, May 10th, 1943, p. 710.

Sample No.	Nature of Enamel Finish	Exposure Period in Weeks	Without Phosphate Treatment	Phosphate Treatment, Method C, with immersion period of :		
				3 mins.	6 mins.	10 mins.
1	Cellulose (two coats grey pigmented cellulose enamel).	0	Initial adhesion moderate.	Initial adhesion good.	Initial adhesion good.	Initial adhesion good.
		13	Adhesion poor, enamel easily chipped or flaked	Unchanged.	Unchanged.	Unchanged.
		26	Further slight deterioration.	Very slight depreciation of adhesion.	Very slight depreciation of adhesion.	Exceedingly slight lowering of adhesion.
		52	Enamel very brittle and adhesion very poor.	Enamel rather brittle but adhesion still fairly good.	Enamel rather brittle but adhesion still good.	Enamel rather brittle but adhesion still good.
2	Stoved Synthetic (red oxide primer and one coat of finishing enamel). Alkyd-urea type.	0	Initial adhesion moderate.	Initial adhesion good.	Initial adhesion good.	Initial adhesion good.
		13	Adhesion deteriorated, enamel flaking on scratch test.	No deterioration.	No deterioration.	No deterioration.
		26	Little further deterioration.	Negligible deterioration.	Negligible deterioration.	Negligible deterioration.
		52	Marked deterioration in adhesion of enamel, flaking badly on scratch test.	Tendency to chip on scratch test, but adhesion still quite good.	Tendency to chip on scratch test, but adhesion still quite good.	Tendency to chip on scratch test, but adhesion still quite good.
3	Air drying synthetic (red oxide primer and one coat of finishing enamel). Oil modified alkyd type.	0	Adhesion very good.	Adhesion very good.	Adhesion very good.	Adhesion very good.
		13	Marked deterioration in adhesion of enamel, flaking on scratch test.	No marked change.	No marked change.	No marked change.
		26	Slight further deterioration.	No marked change.	No marked change.	No marked change.
		52	Adhesion of enamel rather poor.	Enamel hard, but adhesion still good.	Enamel hard, but adhesion good.	Enamel hard, but adhesion good.

Sample No.	Nature of Enamel Finish	Exposure Period in Weeks	Without Phosphate Treatment	Phosphate Treatment, Method C, with immersion period of :		
				3 mins.	6 mins.	10 mins.
1	Cellulose (two coats grey pigmented cellulose enamel	0	Initial adhesion moderate.	Initial adhesion good.	Initial adhesion good.	Initial adhesion good.
		13	Enamel more brittle.	Unaffected.	Unaffected.	Unaffected.
		26	Adhesion deteriorated somewhat.	Unaffected.	Unaffected.	Unaffected.
		52	Enamel embrittled appreciably and adhesion rather poor.	Enamel brittle, but adhesion still quite good.	Enamel brittle, but adhesion still quite good.	Enamel brittle, but adhesion still quite good.
2	Stoved synthetic (red oxide primer and one coat of finishing enamel). Alkyd-urea type.	0	Initial adhesion moderate.	Initial adhesion good.	Initial adhesion good.	Initial adhesion good.
		13	Unchanged.	Unchanged.	Unchanged.	Unchanged.
		26	Marked decrease in adhesion.	Unchanged.	Unchanged.	Unchanged.
		52	Very marked loss in adhesion of enamel, which flaked off on scratch test.	A little chippy on scratch test, but adhesion still fairly good.	A little chippy on scratch test, but adhesion still quite good.	A little chippy on scratch test, but adhesion still quite good.
3	Air drying synthetic (red oxide primer and one coat of finishing enamel). Oil modified alkyd type.	0	Adhesion very good.	Adhesion very good.	Adhesion very good.	Adhesion very good.
		13	Adhesion fairly good.	Unchanged.	Unchanged.	Unchanged.
		26	Adhesion deteriorated and enamel embrittled.	Enamel rather more chippy.	Enamel rather more chippy.	Enamel rather more chippy.
		52	Adhesion of enamel much deteriorated, and only fair.	Enamel rather brittle, but adhesion quite good.	Enamel rather brittle, but adhesion still good.	Enamel brittle, but adhesion still good.

Sample No.	Nature of Enamel Finish	Exposure Period in Weeks	Without Phosphate Treatment	Phosphate Treatment C, for 3, 6 and 10 mins. immersion periods
1	Cellulose.	0	Initial adhesion excellent.	Initial Adhesion Excellent.
		52	Adhesion very good, only very slight tendency for enamel to chip on scratch test or on impact.	Adhesion very good, only very slight tendency for enamel to chip on scratch test or on impact.
2	Stoved synthetic.	0	Initial adhesion excellent.	Initial adhesion excellent.
		52	Condition exactly as cellulose finish.	Condition exactly as cellulose finish.
3	Airdrying synthetic.	0	Initial adhesion excellent.	Initial adhesion excellent.
		52	Some tendency to chip on scratch test or on impact, but adhesion still very good.	Some tendency to chip on scratch test, or on impact, but adhesion still very good.

TABLE XIV.—DURABILITY OF STEEL PANELS, ZINC SPRAYED, WITH AND WITHOUT PHOSPHATE TREATMENT, ENAMELLED, UNDER OPEN ATMOSPHERIC CONDITIONS

(Note.—Enamel finishes as in Tables XI and XII)

Sample No.	Nature of Enamel Finish	Exposure Period in Weeks	Without Phosphate Treatment	Phosphate Treatment C, for 3, 6 and 10 mins. immersion periods
1	Cellulose	0	Initial adhesion on scratch and impact tests excellent.	Initial adhesion on scratch and impact tests excellent.
2	Stoved synthetic	52	Unaffected.	Unaffected.
3	Air-drying synthetic.	0	Initial adhesion on scratch and impact tests excellent.	Initial adhesion on scratch and impact tests excellent.
		52	Very slight chippiness evident on scratch test, but adhesion still very good.	Very slight chippiness evident on scratch test, but adhesion still very good.

TABLE XV.—LABORATORY CHARACTERISTICS OF AIR-DRYING FINISHING MEDIA USED FOR TEST SPECIMENS IN TABLES XIII/XIV

Type	Primer Oil modified glyptal, pigmented red oxide	Finishing Enamel Oil modified glyptal, pigmented grey
Compositional %		
Volatile spirit (loss in weight, 3 hrs. at 110° C.)	32·5	52·5
Total Solids	67·5	47·5
	100·0	100·0
Physical		
Specific Gravity at 25° C.	1·524	0·960
Viscosity in centipoises at 25° C. ..	1,600	820
Drying time (glasslide test) Surface	½ hour	4½ hours
Hard	2 hours	24 hours
Diluent for spraying	25% of turpentine	10–20% of turpentine

corrosion resisting properties of the zinc coating to an extraordinary extent.

From the very brief information presented, it will be seen that much work has been done upon the application of phosphate passivation processes to zinc coatings. Much remains to be done, and this is a fact fully appreciated by the concerns specialising in chemical pre-treatments, and who have already achieved so much in rationalising commercial processes. At the same time, it must not be thought that phosphate passivation will replace chromate treatments. The two pre-treatments should be regarded as complementary rather than competitive. Each has its own merits and its own special sphere of application, although some degree of overlapping may be inevitable. In particular, it can be stated that phosphate coatings tend to be of an electrically insulating nature. They thus interfere with spot welding by electric resistance methods and give high contact resistance, and so are generally unsuitable for dry electrical contact as frequently required in electrical, particularly radio, apparatus. The chromate films on the other hand are only a little higher in contact resistance than freshly plated zinc surfaces, and superior to zinc surfaces after a short period of storage. They do not, therefore, interfere with spot welding and are very suitable for direct dry contact resistance.

Naval Radiographical Laboratory to Assist Welding and Casting Technique
By A. Wilson, (Grad.I.E.E.)

UNTIL 1944 the radiography of welding was carried out in dockyards and shipyards by mobile parties operating from specially equipped pantechnicon vans. These vans consisted essentially of a dark-room for processing films, and storage space for the X-ray set when being transported from one dockyard to another. It was decided in 1944 that laboratories should be constructed in various parts of the country to meet the increasing demand for radiography and the first of these was built in Chatham Dockyard. The plans were drawn up by Naval Construction Department's Radiography Section in conjunction with the various shipyard departments concerned, and building was commenced in the latter part of 1945.

Constructional Details
To ensure that the staff operating the equipment would be adequately protected, it was necessary to construct the X-ray room walls of 14-in. concrete. In order to obtain a material of suitable density to absorb the X-radiation, a mixture comprising 1 part of cement, 2 parts sand and 2 parts rubble was chosen, although this is not structurally the best. Originally no fittings were allowed to be grouted into the wall to a depth of more than 3 in., but an exception had to be made in the case of the conduits carrying the control cables of the 400 k.Vp. set. So that the safety factor might be maintained, conduits were installed at such an angle that the net transverse thickness of wall between the control room and the X-ray beam was of the order of 14 in.

Both entrances to the X-ray room are protected by specially constructed lead-lined sliding doors which are hung in such a manner that even the main doors, which are in the region of 10 cwts. each, can be opened by one person. The door to the control room is fitted with a lead glass window, so that sets may be observed whilst in use, and as a further safety measure all these doors are fitted with interlock switches and relays which prevent the operation of the X-ray sets whilst any of the doors is open.

The dark-room is reached by a labyrinth, the floor of which is set with white tiles to enable the centre path to be followed quite easily. The dark-room itself is divided into a " wet " side for the processing unit, sink, draining boards, etc., and a " dry " side for film storage, and cassette loading. The control room houses the control panels of the sets in use.

X-ray Equipment
At present three sets are in use at Chatham, a Victor OX.400 (250 k.Vp.-400 k.Vp.), which is permanently installed in the laboratory, a Victor OX.250 (60 k.Vp.–

250k.Vp.). and a Philips Macro 150 (60 k.Vp. to 150 k.Vp.). The latter two sets are mounted in special stands, which enable them to be used on board ships and in the various shipyard departments.

With this range of sets it is possible to carry out radiography upon metallic specimens of up to $3\frac{1}{2}$ in. in thickness, keeping within a maximum exposure time of 1 hour. Normal routine exposures on thinner sections are made with an exposure of about 5 minutes, depending upon types of film, intensification screens and film-focus distances employed.

A typical industrial X-ray tube consists of a large pure copper anode, in which is set a tungsten target, and a hot filament cathode, which are enclosed in an evacuated glass envelope. The electrons emitted by the cathode are drawn across to the anode by the large potential difference maintained between the two, and on striking the tungsten target cause an emission of X-rays. By mounting the target at a suitable angle the X-ray beam is directed at right angles to the electron stream and the projected target area is kept very small, whilst having a large heat dissipation area. It is important that the projected area be kept to a minimum as for maximum radiographic definition a point source is desirable to reduce the penumbra effect as much as possible.

Fault Detection

Fault detection is dependent upon shadow formation. When the film is processed, that part which has been acted upon by rays passing through the fault appears darker as the net absorption, assuming that the flaw is of a lower density than the parent metal, is less at this point. The shadow formations obtained for each type of fault encountered are typical of that fault, and after instruction and experience an accurate assessment can be made by the interpreter of the standard of work and the flaws it contains. So that the position of the defects can be located lead markers are placed on the front and back surfaces of the specimen under examination and stereoscopic shots are taken with a source shift of 4 in. to 6 in. From an inspection of the stereoscopic pair in the stereoscope, it is possible to determine the position of a defect with reasonable accuracy.

Auxiliary Mobile Unit

The use of sets on board ships is facilitated by a mobile container which is attached to the laboratory. This consists of a container, based on the road-rail type, fitted with dark-room equipment specially designed by the Naval Construction Department's Radiography Section in the light of experience gained whilst using the pantechnicon vans. In this type of unit the set is stored between the " wet " and " dry " benches, and as the complete unit weighs in the region of 3 tons 10 cwts. it is satisfactorily transported on a flat 5-ton lorry. This container enables processing to be done on site, which is a major factor in a dockyard where a large amount of time would otherwise be wasted in walking to and from the laboratory.

Conclusion

The Chatham laboratory was opened in June, 1946. So far it has been mainly engaged on X-ray work, but gamma ray examinations form part of its service, and it is intended to develop the use of supersonic and magnetic deep fault detection methods. At present, however, the laboratory is fulfilling a necessary function in assisting the development of welding techniques and the maintenance of a good standard of welding in the dockyard generally, and also assisting the foundry in the study of casting techniques.

Welding Medal Competition

COMPETITION for the award of the Sir William J. Larke, K.B.E., Bronze Medal, for 1948, is invited by the Institute of Welding. The Council have decided in the competition for the current year to award a first prize of £50 to the winner of the medal and other prizes totalling £50 to be allocated at the discretion of the examiners.

The competition is open to members, Associate-members, Companion-members, Graduates, Associates and Student-members of the Institute of Welding. Candidates have to submit an original unpublished paper on one or more of the following subjects—gas welding, arc welding or resistance welding, dealing with practical applications embodying specific details of welded work ; welding technique, gas or arc welding ; and design of welding equipment, gas, arc or resistance welding. Entries for the competition should reach the Secretary, the Institute of Welding, 2, Buckingham Palace Gardens, London, S.W. 1, by October 1st. 1948.

Capper Pass Awards

There is a dearth of papers on processes and plant used in extraction metallurgy and of processes and plant used in the fabrication of non-ferrous metals and, with a view to stimulating the preparation of such papers, the directors of Messrs. Capper, Pass & Son, Ltd., Bristol, have offered the Institution of Mining and Metallurgy and the Institute of Metals the sum of £200 per annum for seven years to be applied as follows :—

(a) £100 per annum to be available for one or more awards to the authors of papers on some aspect of non-ferrous extraction metallurgy.

(b) £100 per annum to be available for one or more awards to the authors of papers relating to some process or plant used in the extraction or fabrication of non-ferrous metals ; contributed by persons engaged full time in industry or practice.

The Councils of the Institution of Mining and Metallurgy and of the Institute of Metals have accepted this offer, and have appointed a joint Adjudicating Committee which has power to make the awards on behalf of the two societies and may, at its discretion, make no award or awards of less than the money available if, in its opinion, the quality or number of papers submitted in any year fails to reach a suitable standard. Any sums not awarded will be carried forward to future years.

Papers on extraction metallurgy should preferably be submitted to the Institution of Mining and Metallurgy, while those on processes and plant used in the fabrication of non-ferrous metals should preferably be offered to the Institute of Metals. Both societies are prepared to accept papers of suitable quality from non-members. All papers published by both societies will be examined by the Committee annually, and notices of the Awards will be published in the journals of the two societies and in the Press. The Committee will consider in due course all papers published by the two societies during 1948.

The Metals of the Platinum Group

By C. A. H. Jahn

Platinum, iridium, osmium, ruthenium, rhodium and palladium form the platinum group of metals. The special properties they possess entitle them to be regarded as noble metals. Much detailed information concerning these metals were given by the author in a recent lecture before The Midland Metallurgical Societies which has been abridged in this article.

THE six rarer elements in Group VIII of the periodic system are called the "Platinum Metals" because they occur together in native platinum from which they were first isolated. The metals are platinum, iridium, osmium, ruthenium, rhodium and palladium, and they fall into two distinct sub-groups—the light ruthenian group and the heavy osmium group. They may again be grouped into three pairs according to their vertical arrangement in the Table. The members of each pair have certain characteristics in common and the six metals individually resemble each other in certain respects.

The metals are greyish white and lustrous. They all melt at high temperatures and in the compact form are not acted upon by air or oxygen at ordinary temperatures. Osmium alone burns when strongly heated, forming the tetraoxide, a very poisonous vapour. They are readily reduced from their compounds, which fact probably accounts for their occurrence free in nature. They are found associated with one another in a metallic state in gravels and sands, from which they may be recovered by washing away the lighter material, as in alluvial gold recovery, the resulting platinum concentrates consist of rounded grains or flattened scales.

In 1819 platinum was discovered in considerable quantity in the Urals and these are by far the world's richest mineral deposits. In other parts of the world alluvial deposits have been worked to exhaustion with the exception of those in the South American Republic of Colombia. The principal deposits of the present day in order of importance are the Urals, Colombia and Abyssinia. Ural mineral contains approximately 78% of platinum, Colombian mineral 85% and Abyssinian 72%. Platinum-bearing copper nickel ores found at Sudbury, Ontario and at Rustenberg in South Africa have become important sources of platinum metals.

Modern refining methods achieve an extremely high degree of purity in each of the metals, an example of which is the routine production of platinum 99·99% pure. Copper-nickel ores are first treated by gravity concentration yielding a comparatively rich platinum concentrate which after roasting and acid extraction is treated by the wet process. The table tails from the gravity concentration are subjected to flotation treatment so as to yield a copper-nickel-iron sulphide concentrate containing the remainder of the platinum group metals. This is smelted to copper-nickel-iron matte carrying approximately 48 oz. per ton of total platinum metals, about half of which is platinum. The matte is melted in a reverberatory furnace with salt cake. This is known as the "top and bottom" process in which sodium copper sulphide constitutes the top and nickel sulphide the bottom.

The copper sulphide tops are melted in a reverberatory furnace and from thence are passed to a copper converter where they are blown to blister copper and cast into anodes for electro refining. The nickel sulphide bottoms are ground and roasted in rotary-hearth furnaces to nickel oxide. This is then briquetted with coal, reduced to metallic nickel in a reverberatory and cast into anodes which are refined electrolytically. The adherent slime containing the platinum metals with a fairly large proportion of nickel is removed from the anodes, roasted and treated with sulphuric acid for the extraction of the base metals. The residue containing the platinum metals, copper nickel and lead is treated for complete elimination of base metals, and the platinum metals brought into solution for their separation and individual purification. Thus the principal features of the foregoing treatment are designed to effect a complete recovery of the platinum metals and at the same time yield electrolytically refined copper and nickel.

The melting point of platinum is 1,773° C., and it is obvious that impurities introduced through refractories and gas contamination during melting have to be avoided where the highest degree of purity is to be maintained. The method first employed by Wollaston consisted in compressing the powdered sponge bonded with water into a small brass barrel 1 in. in diameter. The cake was then dried over a charcoal fire and heated in a wind furnace to high temperature, after which the ingot was hot forged and rolled, or drawn into wire. Substantially, the same method for certain applications is in use to-day. Quantities up to 400 oz. are subjected to a pressure of 5 tons/sq. in. after careful packing in a highly polished steel mould. Complete metallising is accomplished by heating to 1,500° C. and forging into a malleable ingot.

For melting platinum, an oxy-hydrogen or oxy-coal gas flame is used through the medium of a blow-pipe, the nozzle of which is made of an iridium-platinum alloy. Another method of melting, much more in use to-day, is by the high-frequency induction furnace in which very high temperatures are rapidly attained. Suitable refractories for this type of furnace involved considerable research before satisfactory results were obtained, but melting is now efficiently conducted in crucibles of zircon or thoria. The ingot is first forged and then rolled at a bright red heat until considerable reduction in section has taken place, after which it is rolled or drawn cold to finished size.

The pure metal is greyish white, soft, malleable and ductile and may be reduced easily to foil or fine wire 0·005 in. diameter. Much finer wire was produced by Wollaston's ingenious method of casting molten silver round a small diameter platinum rod placed centrally in a cylindrical mould, reducing the composite ingot to wire and dissolving away the outer layer of silver in nitric acid. Platinum wire is produced in this way with a diameter of 0·00003 in.

Sheet metal is spun into a variety of shapes and seamless tubing is produced from discs cut from sheet (about 0·1 in. thick and 6 in. diameter) through successive stages of deep drawing on a cupping press and ultimately to drawn tube.

Palladium is melted and worked by methods similar to those employed for platinum. Unlike platinum, however, palladium absorbs large volumes of gas when in the molten state and special precautions have to be taken when melting to reduce gas absorption to a minimum. The pure metal is very ductile though it work hardens more rapidly than platinum. When annealed in air, surface oxidation occurs and a bluish coloration is imparted to the metal. Such oxidation may be effectively eliminated by annealing and cooling in nitrogen which is preferred to hydrogen on account of the well-known affinity for this gas which palladium exhibits when hot.

Iridium and rhodium may be melted and cast by the methods described, except that much higher temperatures for melting and working are necessary. These metals are difficult to work and fabrication is only possible in the initial stages of reduction by forging at very high temperatures. As reduction continues rhodium becomes more amenable to manipulation and the temperature during working may be progressively reduced. In this way it has been possible to produce thin sheet metal and more recently, perfectly sound wire drawn down to 0·004 in. diameter. Iridium has yet to reach that stage of development in fabrication, but by careful working, short lengths of hand-forged iridium wire are now produced. Reduction of size by drawing may ultimately become a possibility, but, at present, short lengths only are stoned and finished by hand with reasonable accuracy of diameter. Manufacture of iridium sheet is less of a difficulty. After forging it may be rolled to accurate limits of thickness and fashioned into various shapes, but the uses of pure iridium are very limited.

As far as is known, ruthenium and osmium have never been satisfactorily fabricated. A major difference between these two metals and others of the platinum group is that the structure of ruthenium and osmium are of the close packed hexagonal lattice type which primarily accounts for the difficulty experienced in working, whilst platinum, palladium, rhodium and iridium have face-centres cubic lattices.

Deville and Debray succeeded in melting small quantities of ruthenium by the blow-pipe, but the only successful method of melting is by the arc furnace using a lime block hearth and taking advantage of the reducing conditions provided by the carbon arc. The temperature reached in a furnace of this type exceeds 3,000° C. Osmium and ruthenium in the molten state and in the presence of air, form poisonous and highly volatile oxides and special precautions have to be taken to avoid injury to the respiratory organs of the operators engaged on this work.

Platinum is the third of the transitional elements in the third long period in the periodic classification of elements, where it lies between iridium and gold and below palladium. Its atomic weight is 195·23 and atomic number 78. The melting point of platinum is 1,773° C., while its boiling point estimated from vapour pressure determinations is in the region of 4,500° C. This high melting point enables platinum to be used for purposes such as furnace windings and laboratory apparatus at temperatures up to 1,500° C. and for immersion thermo-couples in measuring the temperature of liquid steel up to 1,700° C. At temperatures of 1,000°–1,200° C. platinum can readily be hammer welded, while it can be fusion welded by both arc and gas methods. The relatively low coefficient of linear expansion of platinum is responsible for its use in making gas-tight seals through soft glass.

The electrical resistivity of platinum, 10·6 microhms per cm.³ at 20° C., is somewhat higher than the average for the more common pure metals. Although the temperature coefficient of resistivity, 0·0039 per ° C., in the range 0°–100° C. is not unusually high, the consistently high purity in which platinum is available and the reproducibility of its temperature coefficient together with its freedom from oxidation, have led to its adoption as a standard element in resistance thermometry. Similarly, the accuracy and reproducibility of its thermo-electric properties have established the use of platinum against its rhodium alloys as standard thermocouples and of platinum itself as the standard to which the thermo-electric properties of all other metals and alloys are referred.

The mechanical properties of platinum depend upon the condition and history of the specimen. By heavy cold working the Vickers' hardness can be increased from 50 in the annealed state to 120–125 and the ultimate tensile strength from 10 to about 15 tons/sq. in., which falls to 2–3 tons/sq. in., at 1,000° C.

In the electro-chemical series, platinum with a standard potential of 0·86 volt is more noble than silver and palladium, but less noble than gold, iridium and rhodium. Platinum is virtually free from oxide formation and its resistance to a wide range of reagents is not based upon the presence of protective surface films.

In order to meet the full range of industrial requirements, three distinct grades of platinum are available. Grade C is the normal commercial product for all electrical and similar purposes and is usually supplied unless any indication of other requirements is given. It is a specially alloyed platinum, containing 0·5% of another metal of the platinum group in order to increase its hardness and other mechanical properties. To ensure the chemical inertness of platinum for use in chemical plant construction and laboratory apparatus, pure platinum is employed of a minimum purity of 99·99%. For applications relating to thermo-electric measurements a special grade of platinum known as "Thermopure" is employed. The values consistently obtained on this class of platinum correspond with a purity of 99·999%.

Of the six metals of the platinum group, palladium is the second in industrial importance to platinum. It is the lightest of the metals of this group and is outstanding in forming an extensive range of workable alloys with other metals. In the periodic classification it occupies a position between nickel and platinum in Group VIII where it forms the last of the transitional elements of the second long period, between rhodium and silver. Its atomic weight is 106·7 and atomic number 46. The specific gravity is 11·9 compared with 21·4 for platinum.

Palladium has the lowest melting point of all the platinum group metals. The most recent determination is 1,554·4° C., + 1°. Its thermal conductivity is very close to that of platinum, but the specific heat is much greater, being 0·058 against 0·032 for platinum. At

high temperatures palladium loses weight by volatilisation whereas the other metals of the group lose weight by oxidation and volatilisation of the oxides. The coefficient of linear expansion is the highest of the group. Its electrical resistivity is also the highest although only slightly higher than that of platinum, while the temperature coefficient of resistance is the lowest, but again only slightly below the value for platinum. Its ultimate tensile strength, annealed is 12 tons/sq. in. with an elongation of 40%. In the annealed condition it is soft and ductile. Cold working has a considerable effect, heavy reductions increasing the ultimate tensile strength from 12 to about 20 tons/sq. in., the elongation falling from 40 to about 2%. With a standard electrode potential of plus 0·82 volt, palladium is more noble than silver but less noble than platinum. One of the principal characteristics is its ability to absorb large amounts of hydrogen, one effect of this absorption being a marked increase in hardness and strength and a decrease in ductility. The effect is not, however, permanent.

Rhodium, with an atomic number of 45, is the second member of the second series of transitional elements in the periodic system. Its melting point is 1,966° C., and its specific gravity is 12·4. The electrical resistivity of rhodium is slightly less than half that of platinum. Its more important property, from the electrical point of view, however, is its ability to maintain a low and stable contact resistance owing to its complete freedom from the formation of surface films. While the hardness of worked and annealed rhodium is of the order of 100 Vickers, that of electrodeposited rhodium reaches exceptionally high values, ranging from approximately 775–820 Vickers. Its resistance to mechanical wear is very great. Even with heavy pressures and a strong wiping action, very little wear is evident in the rhodium although if a soft metal is used underneath, some depression may be shown if the rubbing surface is small in area. In the electrochemical series rhodium is the most noble of the platinum group metals, but less noble than gold.

Iridium is the second member of the third series of transitional elements and shares with osmium the distinction of being the heaviest known form of matter with a value for specific gravity of 22·4. When heated in air, iridium loses weight at a greater rate than platinum due to the relatively high vapour pressure of its oxide. Iridium is similar to platinum in colour and has been described as having a faint yellow cast. Its melting point is 2,454° C. The hardness of worked and annealed iridium is 220 Vickers and although difficult to work in the early stages of reduction, can, by hot working and frequent annealing at about 1,400° C., be processed into malleable metal. It may be produced direct from powder by cold pressing and sintering, but is the least amenable of the group to this method of consolidation and is readily fractured even after prolonged high temperature sintering. It can, however, be worked through the critical stage and ultimately to sheet or rod having comparable density to that of melted metal. Small amounts of impurities seriously affect the working properties of iridium, but modern refining methods yield an average purity of 99·98%.

Osmium, the first member of the third series of transition elements has a density of 22·4 grammes per cm.[3] and thus joins iridium as one of a pair of the heaviest elements known. Its melting point is believed to be about 2,700° C., but has not been determined. The boiling point has been estimated at about 5,500° C. and is thus the highest of the platinum metals. When strongly heated in air it is oxidised to the volatile tetraoxide. There is no evidence that osmium has ever been worked and the mechanical properties have not been investigated. Its hexagonal structure, apart from its very high melting point makes the acquisition of satisfactory specimens for test a remote possibility. Even at very high temperatures the metal is extremely brittle. The figure of 350 Vickers was obtained on a very pure specimen of the cast metal.

Ruthenium is the first element of the light series of transitional elements having a density a little over half that of osmium. Like the latter, it is characterised by the readiness with which it is converted into volatile tetraoxide. Whilst the vapour is not so virulent in its attack upon the pulmonary organs as osmium, it nevertheless calls for equal care in avoidance of inhalation. Its melting point is in the region of 2,400° C., but has not been accurately determined. On heating the compact metal in air at 1,300° C. it loses weight through volatilisation of its oxide at a rate about 350 times greater than platinum and 700 times greater than rhodium. The metal has never been worked satisfactorily. There is little doubt that ruthenium in the compact form is a very hard metal. As a hardener addition to other metals of the platinum group ruthenium is of great importance. The colour of the metal is similar to that of platinum.

The principal uses of platinum in industry are generally based upon its exceptional resistance to corrosion and consequent stability in critical conditions. The major application of platinum and its alloys in electrical engineering is in the form of contacts where complete reliability of operation is of foremost importance. It is one of the most widely used contact materials in relays and signalling devices carrying small currents. Its resistance to atmospheric corrosion leads to its use as a fuse element in small fuses of very low rating. The ease with which joints can be made between platinum and glass and their reliability at high temperatures account for the use of platinum thimbles to introduce heavy current carrying leads into certain types of radio transmitter valves. Probably the most widely known application of platinum and its alloys in instrument practice is the platinum : rhodium-platinum thermocouple. The wide adoption of this couple is principally due to the characteristic properties of platinum and the fact that the materials can be prepared in a state of exceptional purity. The platinum resistance thermometer provides a precision method of measuring temperatures in the range from − 200°–600° C. and may be used with care at much higher temperatures. It is the most generally corrosion-resistant of all the metals and alloys available to the designer of chemical plant, and it is, therefore, employed where extremely corrosive materials are to be handled or where the purity of the end produce is of great importance. In the manufacture of glass for optical purposes it is essential that the molten glass should not become contaminated with slight traces of oxides. For this reason it has become normal practice to employ platinum vessels since platinum is the only metal which is unattacked by molten glass and which has sufficient strength at the working temperature of about 1,400° C.

The major industrial applications of palladium are based upon its freedom from atmospheric tarnish and its general resistance to corrosion. It is often employed in place of platinum where conditions permit and where first cost is of importance. The applications of rhodium can be grouped into three principal types. These three groups comprise the use of electrodeposited rhodium as a permanent protective finish against atmospheric or marine corrosion, as an electrical contact surface and as a reflecting surface for use either in the visual or the infrared range of radiation. There are very few applications for pure iridium metal, and although relatively hard in the annealed state, its poor malleability and low ductility has diminished the field in which it might otherwise have found uses in keeping with its other valuable properties. The main use of iridium is as a hardening

addition to platinum, of which probably the most important combination is platinum 75% and iridium 25%, used extensively for aircraft magneto contacts. Its applications as a subordinate constituent in a series of alloys with platinum is another of its main uses.

The alloys of the platinum metals fall broadly into two groups—platinum alloys and palladium alloys, and it is from these two series that most of the industrial requirements of the platinum metals are fulfilled. Platinum and palladium as pure metals are similar in their workability characteristics and in their ability to form workable alloys. Of the two metals, palladium forms a somewhat greater range and much use is made of selected compositions from the continuous series of solid solutions which palladium forms with silver, but platinum and its alloys have more extensive applications.

The Vapour-phase Reduction of Arsenic Trioxide by Carbon Monoxide

By R. C. Vickery, M.Sc., Ph.D. and R. W. Edwards

A further investigation on the above subject is described in which it is shown that the vapour-phase reduction of arsenic trioxide by carbon monoxide is possible, and is more rapid than with the solid phase, whilst nearly all theoretical yields of arsenic may be obtained by the method.

IN a previous paper[1] the writers examined the reactions between the solid phases of arsenic trioxide allotropes with carbon and carbon monoxide ; the results then obtained indicated, *inter alia*, that an investigation of the reactions of the vapour phase of arsenic trioxide with carbon monoxide might yield interesting data. These further investigations have now been carried out, the findings being here recorded.

The fundamental idea of the investigation was that, by utilising two gaseous phases instead of a solid/gas system, the reaction would be more rapid and complete owing to the homogeneity of the system, and because of this, the efficiency of the reaction would be higher. Further it was considered that by using arsenic trioxide in the vapour phase, the influence, previously noted, of the allotropic variation in characteristics would be avoided.

Apparatus

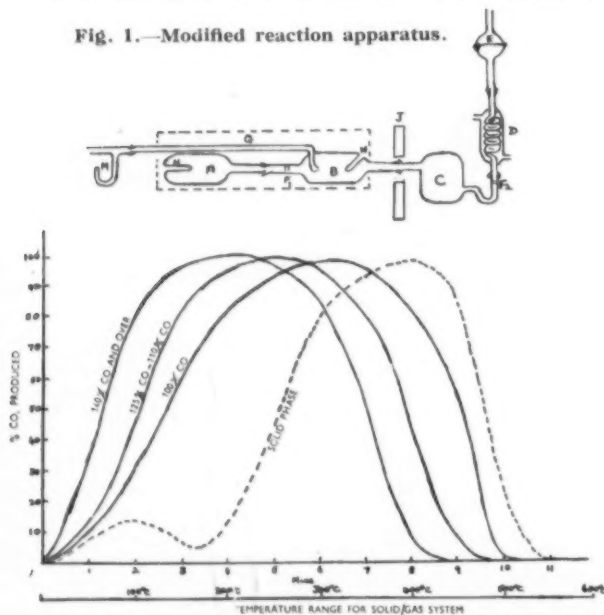The thermal conductivity method previously employed for following the progress of the reaction was again used, but the reaction apparatus used in the past had to be modified (Fig. 1), the assembly being horizontal instead of, as previously, vertical. From the volatilisation cell A, vaporised arsenic trioxide passes via a sintered quartz filter F_1 into the reaction chamber B to which carbon monoxide is supplied via G past a manometer M. It was believed that the reaction in B would be instantaneous at the temperatures employed. The elemental arsenic produced in the vapour phase together with the CO_2 formed as the result of the reaction pass into the condensation cell C, cooled by air blasts. The gas emerging from C is filtered free of solid phases by another filter at F_2, and to ensure the absence of arsenical particles in the gases analysed at E, a short water-cooled condensing spiral was inserted at D.

Temperatures were measured by thermocouples inserted at invaginations at HH. The condensation chamber was protected from radiation and convection heating from the furnace by a silvered asbestos sheet at J. The furnace was of the normal Sillite rod type and the volatilisation apparatus was fabricated from fused quartz.

Fig. 1.—Modified reaction apparatus.

Fig. 2.—Reaction curves obtained for various CO requirements.

1 *Metallurgia*, **36**, 3, 1947.

The arsenic trioxide used was of Analar quality and the carbon monoxide was prepared as before by passing CO_2 over carbon at 800° C. and then through strong caustic soda solution.

Experimental

Having first verified the qualitative validity of the reaction, it was necessary, in order to provide a quantitative basis for this investigation to determine the rate of volatilisation of the arsenic trioxide for correlation with the CO supply. The variation in volatilisation temperatures of the As_2O_3 allotropes was already to hand (see previous paper) so that a minimum temperature at which to observe the effective volatilisation rate was known—i.e., 400° C.

Theoretically, the rate of volatilisation can be obtained by adaption of the Langmuir equation :

$$\mu = p \, (M/2\pi RT)^2$$

or Van Liepmts modification :

$$\log \mu \, (gm \, Cm^2/sec.) = (E/4 \cdot 57T) + \log \sqrt{MT_k/V + 5 \cdot 15}$$

in which equations :

μ = Rate of volatilisation.
p = V.P. of solid phase.
M = Molecular Weight.
E = Heat of sublimation.
T = °K.
V = Molecular volume.

Practical results obtained by noting weight loss with time of a known weight of As_2O_3 whose surface area/gm. had been determined by Andreasens method gave a value of $8 \cdot 72 \times 10^{-5}$ gm./cm.²/sec.—in fairly good agreement with a theoretical value obtained as above of $8 \cdot 53 \times 10^{-5}$ gm.
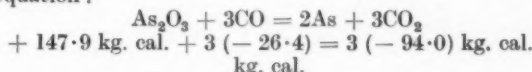
The theoretical volume of CO required is :

$$\underset{\underset{198 \, gm}{}}{As_2O_3} \; + \; \underset{\underset{67 \cdot 2 \, litres}{}}{CO} \; = 2As + 3CO_2$$
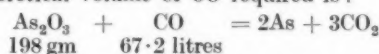
Thus with the volatilisation rate at 400° C. given above, the rate of CO supply required is 24·4 ccs./sec. at N.T.P. and by varying this rate we may obtain varying excesses of CO over theoretical.

According to Mellor[2] reduction of As_2O_3 in an atmosphere of CO takes place at temperatures as low as 60° C. This was confirmed in our previous paper, and in order to discount the effect of this low temperature reaction it was necessary to insert the volatilisation and reaction units into the already hot furnace, the small amount of time then required for the apparatus to heat up being negligible. For comparison purposes, however, a single run starting from room temperature was made ; the progress of reduction is indicated by the broken line in Fig. 2 and compares well with a similar run reported previously. Several runs were then made at 400° C. employing varying excesses of CO. The procedures were as follows : 10 gr. As_2O_3 were placed in the volatilisation cell A which was then connected to B by the ground joint. The assembly was then slid into the furnace already at a temperature of 400° C., and G connected to the CO supply which had already been adjusted to give the required rate of flow. The galvanometer deflections indicating composition of the gas analysed in cell E were then plotted against time. The plottings were made for 100, 110, 125, 140, 150 and 200% theoretical CO requirements, and together with the initial run from room temperature are shown in Fig. 2.

In each of these runs the yield of elemental arsenic obtained was found by weighing C before and after each

2 Compr. Treat. Inorg. Theoret. Chem., Vol. IX.

run. In all cases a little residue remained in A and traces of arsenical material were found in D ; although the residue in A could be weighed and allowed for in yield calculations it was not practicable to weigh D owing to the difficulty of drying the condenser jacket. The figures obtained in the various runs are tabulated in Table I.

In every case it was apparent that the reaction was exothermic by the fact that the thermocouple inserted in B registered temperatures several degrees higher than those observed at A. This is in conformity with the equation :

$$As_2O_3 + 3CO = 2As + 3CO_2$$
$$+ \; 147 \cdot 9 \; kg. \; cal. + 3 \, (-26 \cdot 4) = 3 \, (-94 \cdot 0) \; kg. \; cal.$$
$$kg. \; cal.$$

which shows a value of $(- 213 \cdot 3 - 2 \Delta As)$ in excess on the right-hand side of the equation.

TABLE I

% Theoretical CO Employed	As Yield		Temperature Difference $H_2 - H_1$
	Theory	Actual (corrected)	
100	7·57 grm.	7·5 grm. = 99·0%	10·5° C.
110	7·57 grm.	7·53 grm. = 99·5%	10·0° C.
125	7·57 grm.	7·55 grm. = 99·8%	9·5° C.
140	7·57 grm.	7·56 grm. = 99·9%	9·5° C.
150	7·57 grm.	7·54 grm. = 99·6%	8·0° C.
200	7·57 grm.	7·56 grm. = 99·7%	6·5° C.

It was noted, moreover that the differences in temperatures were dependent upon the percentage excess CO employed (Table I). This is attributed to the cooling effect of the excess gas.

It will be noted in Table I that the earliest approach to theoretical yields of elemental arsenic occurs with 140% theoretical CO, this is attributed to the volume of CO required to replace all air in the apparatus before comparable results were visible by the galvanometer readings.

Summary and Conclusions

That the vapour-phase reduction of arsenic trioxide by carbon monoxide is possible has been shown ; further, that the reduction is more rapid than with the solid phase of As_2O_3 is also proved, whilst very nearly theoretical yields of arsenic may also be obtained by this method. The excess over theoretical quantity of CO required for the reduction is attributed to the volume of gas required to replace air in the apparatus. Conjointly with this, however, it is evident that after allowing for the apparatus volume, an excess of CO increases the initial reaction velocity as indicated by the steepness of the upward slope of the reaction curve (Fig. 2), but apart from this it has little effect upon intrinsic time required for reduction of a given quantity of arsenic trioxide.

The initial " hump " obtained in the reaction curve for the solid/gas system examined previously has been confirmed and the conclusions then drawn on this phenomenon do not require amendment.

Osram Lamps Cost Less

As a contribution towards meeting the present economic situation, The General Electric Co., Ltd., announces that Osram tungsten filament lamps between 100 and 500 watts now cost less as from March 15th.

The reduction applies to both clear and pearl types and, including purchase tax, amounts to 3d. on 100-watt lamps, 4d. on 150-watt, and 8d. on 200-watt. The 300 and 500-watt lamps, which are not subject to purchase tax, are reduced by 6d. and 1s., respectively.

Symposium on the Peeling of Whiteheart Malleable Cast Iron

The occurrence of the defect known as " peel " in whiteheart malleable castings reached serious proportions during the recent war and four papers record the incidence of this defect and show how its causes and the means of elimination were discovered. These papers, together with the report of an investigation on the mechanism of sulphide penetration into steel during carburisation, form a symposium held at a special meeting of the Iron and Steel Institute. Here is given a summary of the papers.

THE peeling of whiteheart malleable cast iron and the penetration of sulphide in the carburisation of steel were discussed at a special meeting of the Iron and Steel Institute, held at 4, Grosvenor Gardens, London, S.W. 1, on April 8th, 1948, with Mr. J. G. Pearce, Director of the British Cast Iron Research Association, in the Chair. The papers presented for discussion included: "The Formation of Peel on Whiteheart Malleable Cast Iron," by A. Preece and K. J. Irvine; "Peel on Whiteheart Malleable Cast Iron," by J. S. Bowden; "Peeling of Whiteheart Malleable Iron," by G. R. Webster and A. E. Probst; "Experimental Work carried out at the British Cast Iron Research Association," by J. Bernstein; and "Sulphide Penetration in the Carburisation of Steel," by A. Preece and K. J. Irvine.

The first four papers were associated with an introduction by Mr. J. C. H. Humfrey, O.B.E., who explained that extensive use of whiteheart malleable iron castings for various military purposes began in 1940; one of the main requirements being for the track links of " carrier " vehicles. Many grey iron founders were called in to increase production of these castings, and kilns and ovens designed for brick and tile manufacture were adapted for annealing them. Many failures of links occurred in service and examination of a number of these showed that failures were, in general, due to: (a) Inadequate annealing; (b) peel; or (c) the development of a brittle, coarsely crystalline, structure due to annealing at too high a temperature.

Apart from peel these defects could be detected by a non-destructive drop test, which was finally applied to 100% of the links, but peel could be detected only by destructive testing, which could be applied to only a relatively small percentage. It, therefore, became very important to find the true causes of peel and what precautions could be taken for its entire elimination. The present symposium collects the results of work carried out and shows how the true cause of peel was established, and the way pointed to a solution of the problem.

Some differences of opinion existed on the influence of ore strength on peel formation. While on the one hand experiments showed that the greatest depth of the peeled layer occurred with the use of strong ores, yet trouble due to peel was considerably less in works where a bright oxidising atmosphere was maintained in the ovens. The problem appears to be very definitely settled by the work of Preece and Irvine, which shows that while sulphur penetration occurs only in atmospheres high in carbon monoxide, yet its segregation to form a subcutaneous layer is dependent on a corresponding depth of decarburisation which must have originally been formed in an oxidising atmosphere.

The malleablising process depends on oxidising conditions in the annealing pots for the major part of the cycle, but gradual weakening of the ore may result in a change to reducing conditions before the cycle is complete, especially if the furnace atmosphere is a reducing one. Given appreciable sulphur content in the ore, such a cycle would appear to be the cause of peel formation. Other factors, such as high sulphur and silicon and low manganese in the white iron, all tend to increase the liability to peel formation.

THE FORMATION OF PEEL ON WHITEHEART MALLEABLE CAST IRON

By A. PREECE, M.Sc., and K. J. IRVINE, B.Sc.

MALLEABLE iron castings having the defect described as " peel " have a perfectly normal appearance and great care has to be taken to prevent such faulty castings passing into service. From works observations there is general agreement that the presence of sulphur in the annealing ore plays an important part in peel formation, but manufacturers differ concerning the particular atmosphere in contact with the casting which is most harmful in this respect. Some contend that the more oxidising the atmosphere the greater the tendency for peel formation, while others hold the opposite view.

It is clear that decarburisation of the iron in the malleablising operation occurs by interaction between the metal and the annealing atmosphere, which consists essentially of carbon monoxide, carbon dioxide, and nitrogen, and usually some gaseous sulphur compound. The balance between the two carbon gases will be controlled by the oxygen pressure of the ore mixture on the one hand and the carbon concentration in the cast iron on the other, and consequently the ratio of carbon monoxide to carbon dioxide will change during the operation. It is thought, therefore, that a clearer insight into the mechanism might be obtained by malleablising specimens of white cast iron in mixtures of carbon monoxide, carbon dioxide, and sulphur dioxide, under experimental conditions in which the gas composition was accurately known throughout the process. This method of examination has proved informative, and in addition to elucidating the main problem, has indicated some interesting features concerned with the diffusion of sulphur in iron.

In the experiments, specimens of cast iron were exposed to mixtures of carbon monoxide and carbon dioxide for 100 hr. at 1,000° C. The effect of an addition

of sulphur to these gas mixtures was also examined in duplicate sets of experiments in which $0\cdot3\%$ of sulphur dioxide was added to each gas mixture. Three cast irons were used in each experiment ; two were in the cast condition and the third had been malleabilised. The analysis of the irons are given in Table I. The first and second were identical except for the sulphur

TABLE I.—COMPOSITION OF IRONS USED.

Iron	C, %	Si, %	Mn, %	P, %	S, %
High-sulphur white iron (as cast)	3·23	0·73	0·22	0·054	0·374
Low-sulphur white iron (as cast)	3·25	0·73	0·22	0·054	0·164
Previously malleable iron ..	—	0·46	0·15	0·061	0·247

content, which is high in one and low in the other. The third iron had been previously malleabilised in an industrial furnace and served to indicate the effect of a previous decarburisation upon peel formation. The structure of the two white irons was normal, consisting of pearlite and cementite ; the malleabilised iron consisted of graphite nodules in a matrix of pearlite and ferrite.

The results obtained from the investigation indicated the conditions which give rise to peel formation and the mechanism concerned. The necessary conditions are :—

(1) The presence of sulphur in the atmosphere surrounding the cast iron.
(2) A highly reducing atmosphere (a high CO/CO_2 ratio).
(3) Partial decarburisation of the white iron.

Absorption of the sulphur by the metal may take place either directly from the atmosphere or from an oxide–sulphide scale formed on the surface of the metal during the malleabilising process. The oxide–sulphide scale can be formed in atmospheres high in carbon dioxide, but it is not until the atmosphere contains less than 15% of carbon dioxide that the sulphur diffuses into the metal. Thus the scale will form during the early stages of the malleabilising process, and later, when the atmosphere becomes highly reducing, the sulphur moves inwards from the surface and forms a band of sulphide at the inner limit of the decarburised zone.

The depth of this band is therefore governed by the extent of surface decarburisation, and factors which influence this will in turn govern the thickness of the peel. Thus an original high sulphur or high silicon content in the iron will tend to give a thick peel, by virtue of the fact that they accentuate decarburisation.

The preferential oxidation of the silicon to give an intercrystalline network of oxide is not an essential accompaniment to sulphur penetration, as has been indicated by the experiments on plain carbon steel. However, since malleabilised cast iron always contains an appreciable silicon content, peeling is invariably associated with the oxide network.

It has been clearly demonstrated that as peel formation requires an extremely high CO/CO_2 ratio in the annealing atmosphere, a simple method of prevention is to be found in the use of ore mixtures containing adequate proportions of ferric oxide.

It follows from this work that the gaseous process for malleabilising will be free from troubles due to peel formation, since the atmosphere in contact with the iron is controlled throughout the operation and will be of constant composition and free from sulphur.

The precise action of carbon monoxide in promoting sulphur diffusion in iron as described in this investigation presents a new and very interesting problem. Much work has already been carried out on this more fundamental question and the results of this further study are summarised from the paper on sulphide penetration in the carburisation of steel by the same authors.

PEEL ON WHITEHEART MALLEABLE CAST IRON

By J. S. Bowden, B.Met., F.I.M.

PEEL, which develops during the malleabilising process, is totally different from the more common scale formed when ferrous metals are heated in air at temperatures in excess of 600° C. It is characterised by the formation of a partially oxidised surface layer of metal of low mechanical properties, in conjunction with a brittle iron sulphide rich film at the peel/metal interface. The outer (peeled) layer, which is largely ferritic with a considerable admixture of non-metallic inclusions such as coalesced oxides, silicates and sulphides, tends to separate from the casting when lightly stressed. Peel buckles readily in compression, and separation of the layers owing to shock or mechanical deformation leads to an appreciable reduction in strength and effective thickness.

Close works' inspection did much to eliminate peeled castings from production, and peel-detection charts reduced the number of peeled links in the service. Modification in design also reduced the risk of failure, but it was considered advisable to discover the causes of peeling and methods of eliminating the defect.

Works' experiments were carried out with this object from which it was concluded that peeling of white heart malleable iron castings occurs when the malleabilising atmospheres contain abnormally high proportions of carbon monoxide. These conditions may be avoided by the use of strong annealing ore mixtures and the maintenance of a mildly oxidising furnace atmosphere. A smoky flame should be avoided and reducing conditions should not occur at any time during the anneal.

The following recommendations concerning metal composition are considered desirable :—

(1) The sulphur content should be as low as possible.
(2) The manganese content should be relatively high, a figure of $0\cdot4\%$ being suggested as an upper limit.
(3) The silicon content should be kept as low as possible, consistent with ready response to malleabilising.

It is considered that the epidemic of peeling troubles which was in certain quarters attributed to the use of Riff ores was primarily due to the use of weak ore mixtures and insufficiently oxidising atmospheres in the malleabilising ovens.

At certain stages of the war there was an acute shortage of hematite ores and the supply position threatened to become desperate. Ore mixtures, which had previously been made up on a 4 : 1 or 6 : 1 basis, were reduced in strength, and additions of new hematite ore were in many cases restricted to the amounts necessary to make up losses in bulk. Some plants found it necessary to add crushed slag, gravel, and other inert media in order to obtain the bulk of packing material. The old practice of " weathering " spent ores for prolonged periods was abandoned through shortage

of ore, and the spent ores went back into circulation without being re-oxidised. Many firms attempted to economise in fuel and to increase pot life by closing down flues and maintaining a sluggish smoky flame.

All these factors contributed to a steady reduction in the strength of annealing ore mixtures and helped to build up conditions favourable to the formation of peel.

PEELING OF WHITEHEART MALLEABLE IRON

By G. R. Webster, A.M.I.M.E., F.I.M., and
A. E. Probst

THE investigation described in this paper consisted of practical works' experiments carried out during the war at a vital period of track-link production when the incidence of peeling was abnormal. The experiments were not intended as part of a planned long-term research programme.

The particular type of peel discussed in this paper is not spread over the whole of the surface of the casting but is of a localised character and can be recognised by small and large metallic " blisters " in lentil-like formation on the surfaces of the castings after their removal from the malleabilising-furnace pots. If these castings are deformed, the lentil-like particles—which may consist of one or more separate layers and which are low in ductility and strength—break away from the surface, and slight, fairly smooth, surface cavities of a grey oxidised appearance remain. In some peeled castings, however, the surface appearance is normal, and the defect is apparent only after mechanical deformation. If such faults occur in isolated positions on large thick-walled castings they can be classified as reducing only the appearance of the piece and not necessarily its engineering usefulness in the final product, whereas with thin-walled castings the peel may form a considerable portion of the total wall thickness. In cases where castings undergo a further surface treatment, such as hot-galvanising, the blisters become detached in the acid pickling bath from the base metal and the resultant galvanised piece shows a corrosion surface-pitted appearance.

Preliminary experiments were carried out to ascertain the effects of high and low sulphur contents in the metal, strengths of ore mixtures, segregation of new ore from spent ore so that the castings were surrounded only by spent ore, etc. In all these experiments peeling still occurred to practically the same degree as in the normal malleabilising practice. Although these experiments had not been conclusive regarding the causes of peeling, they indicated that impurities present in the ore were probably responsible for the phenomenon and further experiments were carried out. The first and second experiments showed that new pyritic ore could cause peeling, the second one in particular showed that peeling can be produced even when the pyritic ore is not in direct contact with the castings. In order to verify the results of these two experiments and to investigate the effect of spent pyritic ore on peeling, 40 castings of the same type, but of different composition, were used in further tests.

A fourth experiment, using stepped test bars, was carried out to investigate the effect of new pyritic ore on malleable iron of various thicknesses and sulphur contents. Very weak ore was used and it was considered

desirable to repeat this experiment using a stronger ore mixture. A sixth experiment was subsequently carried out to determine the loss of sulphur by repeated malleabilising treatments of new pyritic ore (total sulphur approx. 5%) hand-picked from the bulk supply of normal Riff ore.

All the castings and test-pieces used in the experiments to be described were malleabilised in a town's gas-fired continuous bogie-type kiln giving a very even temperature and constant atmosphere. The pots, packed with castings and ore, were sealed and stacked on the bogie hearth. The castings were all packed in the same relative position throughout the experiments, and the malleabilising cycle was as follows :—

Preheating to 980° C.	34 hr.
Soaking at 980° C.	70 hr.
Cooling from 980° to 800° C.	40 hr.
Total time	144 hr.

The results of the experiments are summarised as follows :—

(1) The sulphur content of the new and of the spent ore has a very great effect on peel formation.

(2) The sulphur contents of the particular pieces of ore used were of approximately 5% and 3% respectively, both of which produced peeling to the same extent.

(3) High-sulphur ore produces peeling even if the ore is not in actual contact with the castings.

(4) The extent of peeling is slightly higher when using a strong ore mixture, although differences in the thickness of the peel as produced by a weak and strong ore mixture are not as pronounced as would be expected.

(5) Thin sections of the order of $\frac{1}{8}$ in. are apt to peel more than heavier sections. There definitely appeared to be a certain relation between the section of the casting and the thickness of the peel.

(6) The sulphur content of the metal did not seem to influence the thickness of the peel to any noticeable degree, although metal with a sulphur content of more than $0\cdot28\%$ gave a thinner peel, particularly on heavier sections.

(7) The sulphur content of the Riff ore was very inconsistent. Although the average analysis of a truck varied between $0\cdot12\%$ and $0\cdot2\%$, the sulphur content of some hand-picked pieces of ore was as high as 5%.

The authors state that no definite explanation can be given as to the mechanism of peeling as produced in these experiments. It is known that iron pyrites (FeS_2) gives up sulphur when heated in an oxidising atmosphere above a certain temperature. It also appeared that the ferro-sulphur as used in experiment 1 was oxidised by the pot atmosphere, probably to SO_2. However, SO_2 is a reducing agent, and one would therefore not expect that it would attack the metal during the malleabilising process.

It is beyond doubt, however, that the high sulphur content of the Riff ore was the main cause of peeling. It can also be stated that peeling would not have disappeared so long as this ore had to be used in malleabilising, although the extent of the peeling could be reduced by diluting the spent ore with granite chippings.

EXPERIMENTAL WORK CARRIED OUT AT THE BRITISH CAST IRON RESEARCH ASSOCIATION

By J. Bernstein, A.R.I.C., A.C.T.C., A.I.M.

FROM a brief review of the literature, it is obvious that the formation of peel is related to the formation of a sulphide concentration some distance from the surface of the casting. The first object of the present author's experimental work was to demonstrate that this sulphide concentration was due to the use of ores of high sulphur content. Work was carried out to study the progressive formation of the peeled layer during the annealing treatment. This was followed by a study of the various factors which encourage or inhibit peeling. Much of this work was carried out by annealing in conventional ore mixtures, but it was ultimately extended to cover annealing and decarburisation under gaseous conditions in the absence of ore. Many subsidiary experiments were carried out and are described in the paper.

Following the experimental work, specific examples are given of some of the results obtained arising from variations in the metal composition and in the sulphur content of the ore. These examples are followed by a generalisation of the influence of these variables which is considered to be permissible in the light of the experimental evidence.

(1) In an iron of base composition: Total carbon 2·2%, manganese 0·39%, sulphur 0·093%, and in which the silicon contents were increased by stages of 0·3% from 0·5 to 1·7% of silicon, peeling was produced in all bars when the amount of sulphur in the annealing ore was 1%. The amount of peel present increased as the silicon content of the metal increased. When bars of the same chemical composition were annealed in ore containing 0·4% of sulphur, peeling occurred only when the silicon content exceeded 1·4%. The results also indicate that high silicon contents will, even in the presence of excess manganese, induce peeling, provided that the sulphur content of the ore is sufficiently high.

(2) Peeling was also formed when test-bars of base composition: Total carbon 2·3%, silicon 1·3%, sulphur 0·093%, and in which the manganese content was increased from 0·14 to 1·47%, were annealed in ore containing 1% of sulphur. The amount of peel decreased as the manganese content of the metal increased. When bars of the same chemical composition were annealed in ore containing approximately 0·4% of sulphur, peeling occurred only when the manganese content of the metal was 0·14% and 0·39%. Manganese contents in the metal above this latter figure completely inhibited the formation of peel.

(3) In an iron containing 3·1% of total carbon, 0·55% of silicon, 0·096% of sulphur, and manganese contents increasing from 0·16 to 1·34%, no peeling occurred when test-bars were annealed in ore containing 0·30% and 1% of sulphur.

(4) In an iron of base composition: Total carbon 3·2%, silicon 0·57%, manganese 0·29%, and in which the sulphur contents were increased from 0·21 to 0·42%, peeling occurred when test-bars were annealed in ore containing 1% of sulphur, the depth of peel increasing with increasing sulphur in the metal. When the sulphur content of the annealing ore was between 0·4 and 0·5%, traces of peeling were observed only when the sulphur content of the metal exceeded 0·3%.

In these experiments it was again confirmed that peeling occurred only when the annealing ore contained appreciable amounts of sulphur. Under these conditions the following factors were found to influence the severity of the peeling and the depth of sulphide penetration when a wide range of chemical compositions was considered :—

(a) The actual sulphur content of the ore. (The higher the sulphur content, other conditions being the same, the deeper the peel.)

(b) The ratio of manganese to sulphur in the metal. (The higher this ratio, the lower is the tendency to peel.)

(c) The silicon content of the metal. (The higher the silicon content the greater is the tendency to peel.)

(d) The initial carbon content of the metal. (The higher the carbon content, the lower is the tendency to peel.)

Factors favouring the formation of peel also increase the depth of the peel and sulphide penetration when peeling occurs. Other variables, such as ore strength, time of annealing, and annealing temperature, are known to influence peeling, and these are dealt with elsewhere in this paper.

It should be borne in mind that these conclusions are based on the results of experiments covering much wider variations in chemical composition than are normally experienced in the commercial manufacture of whiteheart malleable iron. For instance, the widest range normally covered is probably 2·8–3·7% of total carbon, 0·3–0·8% of silicon, 0·1–0·5% of manganese, and 0·07–0·4% of sulphur. Day-to-day variations in individual works are, of course, usually confined within still narrower limits. With this in mind, the author is inclined to attach more importance to variations in the manganese and sulphur contents of the metal and the sulphur content of the ore than to variations in the total carbon and the silicon contents of the metal. In any given case, all the factors influencing the formation of peel function simultaneously. The general statements made above are qualitative only, and it would, for instance, be impossible at the present stage to indicate a precise safe maximum value for the sulphur content of an ore for annealing metal of a given composition. However, it is felt that for normal practice the sulphur content of the ore should not exceed 0·25%, but if this figure cannot be maintained, freedom from peeling may be achieved by the use of manganese contents in excess of those required to balance the sulphur, according to the formula : Manganese (%) = 1·7 × sulphur (%). This applies only for normal low-silicon contents.

SULPHIDE PENETRATION IN THE CARBURISATION OF STEEL

By A. Preece, M.Sc., F.I.M., and K. J. Irvine, B.Sc.

IN the first paper of this symposium, the authors described the formation of a band of iron sulphide some distance below the surface of a specimen of cast iron. The structure resembled that obtained in commercially malleabilised cast iron when the defect known as "peeling" occurred. It was shown that on exposing the iron at high temperature to a carbon-monoxide/carbon-dioxide atmosphere containing sulphur

a scale which contained iron sulphide formed on the surface. This iron sulphide could be made to move into the metal by a subsequent exposure of the specimen to a carburising atmosphere.

Although it was possible to lay down the conditions governing peel formation, the actual mechanism by which the sulphide moved into the metal was by no means clear. Further experiments have therefore been carried out to investigate this problem.

The experiments were carried out primarily to investigate the action of carbon monoxide in causing the sulphide to move into the metal, and also to explain the various aspects of the structure, namely, the definite band formation and its association in some cases with an intercrystalline network of oxide or silicate.

Experiments, in which suitably coated specimens of Armco iron were exposed to carburising mixtures of carbon monoxide and carbon dioxide, have demonstrated the mechanism of sulphide penetration into steel during carburisation, and by adjusting the gas mixture in contact with specimens, deep-seated iron sulphide inclusions have been converted to iron oxide. Iron sulphide inclusions have also been converted into manganese sulphide by prolonged treatment at 1,000° C. The results of this investigation also show interrelated effects between carbon, sulphur and oxygen which may be of significance in the segregation and homogenisation of steel castings.

The authors' views on the results of this investigation are very informative. They state that the results have shown that sulphide penetration into steel under carburising conditions involves first the formation of a molten sulphide on the surface which enters the metal as such by virtue of the fact that it dissolves iron on one side and rejects it on the other. The rate of penetration is thus governed by the diffusion of iron through the molten sulphide, and this is in turn controlled by the difference in carbon content on either side of the sulphide.

The fact that the penetrating layer must be molten fixes the lowest temperature for penetration at the melting point of the iron/iron-sulphide eutectic, i.e., 985° C.

The following two observations support the claim that the penetrating sulphide can carry oxygen in solution :—

(a) When the sulphide band was formed in the presence of oxygen the lowest temperature for penetration dropped to 960° C.
(b) With high-silicon steels the sulphide band was associated with internal oxidation.

The general effect of carbon, manganese, and silicon in the iron is to decrease the rate of penetration. These elements increase the degree of dispersion of the sulphide band, and when this reaches a stage where the latter no longer presents a barrier to the carbon, penetration of the sulphide ceases.

The conversion of the deep-seated layer of iron sulphide to oxide by simply maintaining a suitable oxygen pressure at the surface of the specimen is interesting, especially as this can occur at oxygen pressures too low to oxidise the iron. Similar processes may operate in the embrittlement of steel on heating in atmospheres of low oxygen pressure, as it is possible that other compounds existing at the boundaries may be oxidised in a similar manner.

The results also show interesting related effects between the three elements carbon, sulphur, and oxygen which may be of significance in the segregation or homogenisation of steel. The rapid diffusion of sulphur to regions high in oxygen which has been indicated in this work may offer some guidance in solving the problems concerned with the overheating of steel.

The International Nickel Company

The report of the above Company and its subsidiaries, recently issued for the year ending December 31st, 1947, shows a net profit in terms of U.S. currency of $33,503,466 after all charges, depreciation, depletion, taxes, contigencies, etc., equivalent, after preferred dividends, to $2·16 per share on the ordinary stock. In his statement to shareholders Mr. Robert C. Stanley, chairman and President, said there was a steady demand for the company's products during the year. Sales of nickel in all forms, 205,278,868 lb., were the highest of any peace-time year except 1937. Sales of copper, 220,671,157 lb., were the highest in the post-war period. Sales of platinum metals, 191,761 ozs., were considerably lower. Included in the year's sales were 43,184 ozs. of gold, and 1,384,384 ozs. of silver.

Mines and smelters operated continuously, although handicapped by an acute man-power shortage which lasted from April to October. Technical research directed towards improvements in mining methods and in plant processes, was carried on at an accelerated rate ; this is of major importance in counteracting the upward trend in operating costs. Completion of the new process plant at Copper Cliff was again delayed by deferred deliveries of materials and by man-power shortage. Apparently the various units of this plant will be ready for operation before the year's end.

In concluding his report to shareholders, Mr. Stanley referred to the future outlook, emphasising the need for nickel and nickel alloys for industrial projects held up during the war years and to the restoration work to be done following the destruction brought about by the war. These are continuing needs, and it is a major responsibility to assure adequate supplies of nickel and nickel products to meet these demands. To this end the Company's exploration and development worl and mines development programme are being accelerated. Improvements in the Company's smelters, refineries and rolling mills are being made in accordance with production requirements, experience, and research.

A number of factors, however, make it difficult to forecast continuous prosperity. Inflation is probably the most important of these, which can only be overcome by far-seeing statesmanship and by united efforts on the part of industry, labour, and the public to bring about stabilisation of the wage-price structure. Another factor is the employer-employee relations, which should not be too difficult of solution once the problem of inflation is properly solved ; there is no sound reason why industry and labour should not be able to solve their own differences in a spirit of amity. The European recovery programme is also of major importance ; on it hinges the peace and prosperity of the world. To make this programme successful will require a wider degree of co-operative statesmanship, and a greater degree of self-sacrifice on the part of all peoples, than the world has known. The accomplishment of a just and durable peace is too vital to all for it not to succeed.

Modern Methods of Gas Analysis[*]
Part VIII—Detection and Estimation of Impurities in Industrial Gases
By W. D. Vint

Gas analysis apparatus described in previous sections have certain limitations in estimating such impurities as NH_3, H_2S, SO_2, etc., and there are many instances where their determination is necessary. A choice of several methods usually exists and some are described in the present article.

THE types of gas analysis apparatus described in foregoing articles have certain limitations when the question arises of the estimation of such impurities as NH_3, H_2S, SO_2, etc. These latter gases are always present (usually in small amounts) and sometimes give rise to a number of defects in the heating and treating of metals. To quote a few examples—an abnormally high sulphur content in a producer gas can cause billets to stick in the furnace and impair the surface of the steel, and high sulphur contents in any heating gases cause corrosion of metallic parts which happen to be in contact with the waste gases. Another example is that of the grey mottled surface defect produced when H_2S is present in atmospheres used in the bright annealing of steel products. More examples could be quoted concerning the derogatory effect of unwanted impurities, but the three cases mentioned should make it evident that an accurate knowledge of the nature and extent of adulterating gases present in different fuels is of inestimable value when comparisons are to be made.

A choice of several methods usually exists for each of the following impurities and in such cases only the simplest and most reliable methods will be mentioned.

Hydrogen Sulphide (H_2S).—H_2S is rarely present in a gas to the complete exclusion of SO_2 and under these circumstances alkaline reagents cannot be used. Practically any metallic salt in aqueous solution which will precipitate a metallic sulphide soluble in HCl provides a suitable reagent. Cadmium Chloride solution is the usual reagent employed and the gas is passed through the solution in a slow steady stream until a definite yellow precipitate has formed, the volume of gas noted and converted to N.T.P., then the solution is titrated with N/10 standard iodine solution using starch as indicator.

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[*]Continued from January, 1948 issue, page 152.

1·0 Iodine sol. is equivalent to 0·112 ccs. of H_2S.

H_2S may also be estimated by passing the gas through a standard solution of iodine. Small quantities can be determined colourimetrically by the use of p–amino dimethylanaline.

A further method for the determination of H_2S makes use of the apparatus as shown in Fig. 1. The bulb possesses an elongation of such dimensions that two graduations may be marked on it, the first at 150 ccs. and the second, 20 ccs. below. The bulb is provided with a three-way tap at the top and a single-way tap at the bottom. Attached to one of the outlets at the bottom tap is a 10 ccs. cylinder graduated in tenths of a cc. and the bottom outlet serves as a connection for the levelling bottle. Gas is introduced into the apparatus in the usual manner and adjusted to atmospheric pressure, the levelling bottle is attached and the gas brought to reduced pressure by lowering the level of the liquid to the second mark. The enclosing liquid is 0·1% starch solution. N/50 iodine is then run in from the graduated cylinder and a titration performed to a slight permanent blue colour.

No. of ccs. iodine $\times$ 100 = Grams H_2S per 100 cub. feet.
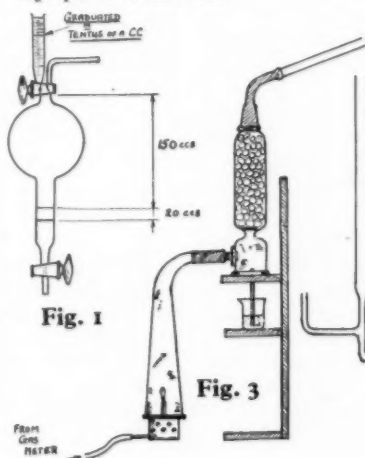
1 cc. of iodine = 50 grains S per 100 cub. feet.

A quick qualitative test for H_2S is made by placing a piece of paper soaked with lead acetate solution in the gas. Blackening of the paper indicates the presence of H_2S.

Ammonia (NH_3).—On account of the extreme solubility in water and dilute acids the problem of the detection and estimation of NH_3 is a fairly simple one. The apparatus and connections are the same as those employed in the first H_2S test. The strength and quantity of acidic solution depends upon the amount of NH_3 present and the volume of gas passed through. A few drops of methyl orange should be added to the solution and the stream of gas should be stopped before the colour changes to yellow. The solution can then be back titrated with sodium carbonate solution of the same strength and the number of ccs. acid neutralised by the NH_3 calculated. From the fundamental equation, using sulphuric acid, $1\cdot0$ cc. N/10 $H_2SO_4 = 2\cdot24$ ccs. NH_3, the NH_3 percentage may be calculated.

Sulphur Dioxide (SO_2).—A quantitative determination may be made by absorbing the gas in standard iodine solution and back titrating with standard sodium thiosulphate solution.

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI.$$

Fig. 1

Fig. 3
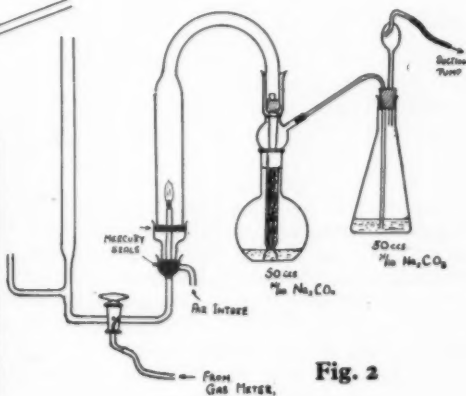
Fig. 2

From the equivalent—1 cc. N/10 iodine $= 1\cdot12$ ccs. SO_2, the latter percentage may be calculated.

Sulphur dioxide may be estimated qualitatively by the bleaching of iodo-starch paper or fuchsin paper.

Total Sulphur Estimation

The valuation of a particular supply of town or coke oven gas depends very largely upon the total sulphur content and in view of the undesirability of this element, great efforts are made at the gas works or coke oven plant to remove it. In the gas itself sulphur exists as a variety of compounds such as H_2S, SO_2, CS_2, and in other complex organic compounds. There is no easy convenient way of estimating these compounds so the gas is simply burnt and the sulphur which has all been converted to SO_2 is absorbed in iodine or alkaline solution.

Figs. 2 and 3 illustrate two methods by which the test is made. The method of metering the gas is the same in each case but it should be borne in mind that gases containing abnormally high sulphur contents (and in which cases a certain quantity of water soluble sulphur compounds are present) should be measured by passing through a dry meter.

In Fig. 2, the gas is metered, burnt in an inverted U tube with a mercury seal and the products of combustion passed through a measured amount of standard sodium carbonate solution. When about half a cubic foot (this depends upon the sulphur content of the gas) has been burnt, the gas is shut off and the apparatus allowed to draw air over for about three minutes. When cool, the apparatus is dismantled and the contents of the scrubber added to the flask and washed two or three times. The solution is then titrated with standard sulphuric acid solution and the percentage of sulphur calculated.

1 cc. N/10 $Na_2CO_3 = 0\cdot0016$ grams. S

Strong caustic soda solution may be used instead of standard sodium carbonate and the sulphur may then be estimated gravimetrically by precipitation with barium chloride.

In Fig. 3 the seal at the base of the combustion chamber is ammonia and air is drawn through holes surrounding the burner. Small pieces of solid ammonium carbonate are sprinkled round the burner so that air is mixed with ammonia before it reaches the flame. The oxidised sulphur compounds combine with the ammonia and are retained by the tower which

has been previously thoroughly wetted with distilled water. The products of combustion are drawn upwards by the action of the chimney (not shown fully in the sketch but is about eight feet long) and fresh air is drawn in at the burner. The flame should be as small as possible and fully oxidising otherwise sulphur compounds can pass through the apparatus unaffected.

When a fair quantity of the gas has been burnt the flow is stopped and the apparatus allowed to cool. The tower, small beaker, chimney and seal are now all washed into a 600 ccs. beaker to which is added a few drops of bromine. The contents of the beaker are now brought to the boil and made acid with HCL. When the bromine fumes have cleared barium chloride solution is added and the sulphur estimated as $BaSO_4$.

Detection and Estimation of the more Uncommon Gases

Nitrogen Peroxide NO_2 or Nitrogen Tetroxide (N_2O_4).—By absorption is standard $KMnO_4$ solution in the presence of H_2SO_4.

$$10NO_2 + 2KMnO_4 + 3H_2SO_4 + 2H_2O = 10HNO_3 + K_2SO_4 + 2MnSO_4.$$
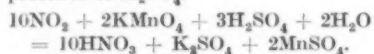
A qualitative test may be made by absorbing in an alkali and testing for nitrates or by the use of iodo starch paper.

Hydrochloric Acid Gas (HCl).—By absorption in a standard alkali.

The qualitative test is made by bringing the gas into contact with ammonia when dense white fumes are produced. (Note.—The gas is extremely soluble in water, therefore wet methods of metering cannot be used.)

Hydrocyanic Acid (HCN).—The gas may be dissolved in water or a standard alkali and the solution tested for cyanides.

Phosphine (PH_3).—The quantitative determination of the gas may be made by burning the gas and subsequent oxidation with bromine to phosphoric acid. This may then be precipitated to magnesium phosphate by the addition of a soluble magnesium salt in ammoniacal solution and the precipitate weighed.

1 cc. of $PH_3 = Wt$ of $Mg_2P_2O_7 \times 201\cdot25$.

A qualitative test for PH_3 is by the blackening of silver nitrate paper. The test can only be carried out in the absence of gases soluble in KOH.

Nitric Oxide (NO).—Ferrous sulphate solution acidified with H_2SO_4 may be used to absorb the gas.

Acidulated $KMnO_4$ is another reagent which may be used. The gas may be tested qualitatively by absorbing in H_2O and testing for nitrites.

Acetylene (C_2H_2).—The gas may be estimated quantitatively by absorption in either bromine water or fuming H_2SO_4. It may also be determined gravimetrically by passing into ammoniacal cuprous chloride solution when a reddish precipitate of copper acetylide is formed. The precipitate which must not be allowed to become dry is washed free from copper salts, dissolved in HCl and estimated colourimetrically or otherwise in a similar manner to the method employed for copper in steel.

The qualitative test may be made by passing the gas into ammoniacal cuprous chloride solution.

Determination of Moisture in Gases

Generally speaking, the gas is passed through an absorption bulb containing a suitable dehydrating reagent. The bulb is weighed before and after and the difference in weight divided by the volume of gas passed through represents the moisture content per unit volume.

The choice of a dehydrating reagent is important and the following facts should be borne in mind.

(1) The reagent must not react chemically with the gas.

(2) It must not absorb the gas.

The following reagents are generally used for moisture estimations :—

Calcium oxide.
Phosphorous pentoxide.
Calcium chloride.
Alumina.
Magnesium perchlorate.

Most of these may be classed as either acidic or basic and a good rule to follow is that the gas passed over should not have opposite characteristics, e.g., calcium oxide or alumina could not be used for CO_2 or SO_2, and phosphorus pentoxide would be unsuitable for NH_3.

The reagents as listed possess certain degrees of dehydrating properties—phosphorus pentoxide is more powerful than magnesium perchlorate and the latter is more powerful than calcium chloride.

A small point of accuracy which is often overlooked in the actual determination is that the first weighing of the absorption bulb should be made with the bulb full of the gas in which the moisture determination is to be made.

Iron and Steel Specifications in Russia

American methods seem to have been largely adopted by manufacturers of iron and steel in Russia, according to recently published technical literature in that country. Russian specifications indicate that manganese in steel compositions is used more than in this country or in the United States, whereas the elements molybdenum and cobalt are used less. It is noteworthy that the specification marks used for some steels give an approximate indication of the constituents.

DURING the war period and despite the obvious difficulties, a few books on various branches of metallurgy were published in Russia, such as those of N. F. Bolkhovitinov on grain size and properties of steel (1943), A. A. Bochvar on physical metallurgy (1945), A. C. Zymovski on metals and alloys in electrical industry (1941), N. A. Minkevitch on high speed cutting steels (1944), G. N. Troitski on cast irons (1941), and a few others. Since the war, the first named author, Bolkhovitinov, has completed another work on the physical metallurgy and heat treatment of steels (Moscow 1946) which also includes substantial sections on cast and malleable irons, as well as non-ferrous alloys. It contains a lot of information in comparatively small compass, including frequent references to American practice—which is evidently closely studied in Russia—and more particularly numerous extracts from Russian official (GOST) iron and steel specifications, giving the elemental composition of a large number of constructional and other steels. Incidentally, the author considers that manganese is more largely used in his country for steel manufacture than in America, since that particular element is more abundant in Russia. But he thinks the converse is the case in respect to molybdenum and cobalt.

The Russian specification governing constructional steels, used mainly without special heat treatment, is GOST 380/41, and for special steels heat-treated, GOST V.1050/41. This latter includes two series of manganese steels, one with a comparatively high content of Mn, up to $1\cdot8\%$, and the other the more normal steel, with Mn content from $0\cdot25$ to $0\cdot75$. The former carry the following marks :—

High Manganese Steels
{
$0\cdot70$–$1\cdot00\%$ Mn : 15 G, 20G, 30G, 40G, 50G and 60GM
$0\cdot90$–$1\cdot20\%$ Mn : 65G and 70G.
$1\cdot20$–$1\cdot60\%$ Mn : 10G2.
$1\cdot40$–$1\cdot80\%$ Mn : 30G2, 35G2, 45G2 and 50G2.
}

The low manganese steels are called "modified constructional carbon steels with normal manganese content," with limits of Mn as above, limits of carbon from $0\cdot05$ to $0\cdot75$, and a silicon content of $0\cdot15$ to $0\cdot30$, except in the first (No. 08) in which the Si is up to $0\cdot03\%$. These low Mn steels also have a sulphur limit of $0\cdot055\%$, phosphorus $0\cdot045\%$, nickel $0\cdot30\%$ and chromium $0\cdot25\%$. After the first (08) the marks form an arithmetical progression : 10, 15, 20, etc. up to 70.

At this stage, it may be pointed out that the Russian specification marks give an approximate quantitative indication of the constituents of the iron or steel, in certain classes. Thus : Kh = chromium, G = manganese, N = nickel, Ph (or F) = vanadium, M = molybdenum, V = tungsten, Yu = aluminium, S = silicon, D = copper, K = cobalt, and T = titanium. These letters by themselves indicate at least 1% of the element, and are preceded by two figures to represent the carbon content (in hundredths per cent., i.e., 12 = $0\cdot12\%$). Therefore a mark 12KhN3A, represents $0\cdot12\%$ carbon, about 1% chromium, and about 3% Ni, the A indicating a sub-class. Mark 15KhPh means $0\cdot15\%$ carbon, 1% chromium and, in this case only $0\cdot2\%$ vanadium, so it hardly seems to conform with definition ; nor are the marks always fully descriptive, as indeed could hardly be expected.

This method of marking is compared with the American AISI–SAE. The American specifications are said to differ from the Russian in having closer limits of carbon content, which is of considerable convenience in heat treatment and ensures more definite stipulation of casting or heat treatment conditions. On the other hand, it is also thought that, in many cases, the American specifications are much too numerous, thus adding to the difficulties of manufacture.

In regard to steels for cutting tools and instruments, these mainly come under GOST V.1414/42, particularly the A series (A12, etc.). A12 contains $0\cdot08$–$0\cdot16\%$ C $0\cdot08$–$0\cdot20\%$ sulphur, and $0\cdot08$–$0\cdot15\%$ phosphorus, whilst A20 has $0\cdot15$–$0\cdot25\%$ C, $0\cdot8$–$0\cdot15\%$ S, and no more than $0\cdot06\%$ P. These are the so-called automatic steels with relatively high sulphur and phosphorus content. They are largely used in Russia for agricultural machinery and must be easily worked.

Grey cast irons are governed by GOST V.1212/42, containing from $1\cdot7\%$ carbon, and comprising the Sch series, with Brinell hardness from 143 to 241, and with fairly extensive diffusion of relatively large graphite grains. A rough classification of graphitic grain size is given in OST 26049 as follows :—

G1, Large, above 300 mu   G4, very small
G2, Medium, 150–300 mu   G5, pin points
G3, Small, 80–150 mu

Other grades are G6 and G7, according to shape ; and G8, G9 and G10, according to distribution. This official standard No. 26049 also includes a classification of the phosphorus eutectic, according to the extent and nature of its diffusion, namely E1–E5.

Malleable cast irons are widely used in Russia, and when properly made from the so-called white irons they have high strength and hardness. The cementite of the white iron transforms into graphitic structure with increase in tensile strength and workability. This type is largely used in automobile and tractor works, also for agricultural machinery and armour plate. Bolkhovitinov says that the manufacture in Russia of pearlitic malleable iron by European methods is now hardly extant even in the oldest factories, and has nearly everywhere been replaced by American methods which yield a better product at lower cost. Special reference is made to the Duplex method of General Motors and to the data on malleable irons issued by the A.S.T.M. It may be

mentioned here that the effect of graphite in white cast iron has been studied in recent years by K. P. Bunin and others, and results published in *Trudy Ural*, etc., 1944, 19, 80–6, with special reference to the effect of accelerated cooling by pouring the molten iron into ice-water. As a matter of fact, the particular structure of white irons is largely due to rapid cooling. In regard to malleable irons generally, it may be useful to compare the paper read by H. A. Schwartz before the Amer. Foundrymen's Assn. early this year.

The chrome-manganese steels naturally figure prominently among Russian constructional steels, and are divided into two classes : modified steels and high modified steels. In both classes, the carbon content is 0·10 to 0·55%, the chromium 0·60 to 1·75, and the manganese 0·30 to 1·20%. Most of them also contain some nickel, over a fairly wide range, namely 0·10 to 4·60%, examples therefore of some of these steels with their relevant marks are :—

1. *Modified Steels :*

	C	Mn	Si	Cr	Ni
15Kh	0·10–0·20	0·30–0·60	0·15–0·30	0·70–1·0	less than 0·30
20KhG	0·15–0·25	0·90–1·20	0·15–0·30	0·90–1·20	less than 0·30
15KhPh	0·12–0·20	0·30–0·60	0·15–0·30	0·80–1·10 and VO·10–0·20	less than 0·30

2. *High modified steels :* (A) type

	C	Mn	Si	Cr	Ni
30KhMA	0·25–0·35	0·40–0·70	0·15–0·30	0·80–1·10 and M 0·15–0·25	less than 0·30
12Kh2N4A	below 0·17	0·3–0·6	0·15–0·30	1·25–1·75	3·25–3·75

It will again be noted that elements are sometimes included in the mark although considerably less than 1% in content. The second or A class also includes two or three with tungsten and a few with aluminium (from 0·80 to 1·25%). (The complete tables can be supplied if required.)

Steel research in Russia is, of course, largely concentrated on heat treatment, and among these the Cr–Mo–Al appear to be of special interest. I. E. Brainin has recently investigated the thermal treatment of one of the above-named chromium steels, 38KhMYuA, which no doubt is the same as the 35KhMYuA given in the table, the carbon content of which goes up to 0·38%. Results are recorded in *Stal*, 1945, 67–77. In regard to the effect of preliminary heating on crystal growth, mechanical properties, and the appearance of a stone-like fracture in this steel, it was found—as might indeed be anticipated —that crystal growth is a direct function of temperature of preheating. Intensive growth of grains started at 1,000° C. There was no relation between preliminary heating and impact strength : but the smaller the MoO–E grain size, the greater the impact strength.

Among the few low alloy steels, of which the composition has lately been given, may be mentioned the so-called DS (Dvortsa Sovet, or Soviet Palace) steel, and the Korten, Manten, Miari P and Naks steels, the composition of which is as follows :—

	DS	Korten	Manten	Miari P	Naks
C	0·12–0·22	up to 0·12	up to 0·30	up to 0·12	0·10–0·11
Mn	0·7–1·1	0·1–0·5	1·1–1·6	0·5–1·0	0·6 –0·75
Cu	0·4–0·7	0·3–0·6	up to 0·2	0·5–0·7	up to 0·25
Cr	0·4–0·6	0·5–1·5	—	0·2–1·0	0·5 –0·65
Ni	—	up to 0·55	—	0·25–0·75	0·1 –0·25
P	up to 0·01	0·07–0·2	up to 0·4	0·08–0·12	up to 0·04

Particular attention is being given to special purpose steels, e.g., for gears, crankshafts, ball bearings, cutting tools, agricultural machinery, especially tractors and so forth. Gear steels are classified under six headings, the first four of which include the following (with corresponding American types in brackets) :—

1. Alloy steels with 0·45–0·50% carbon, such as 40Kh (A5140), 45KhN (A3145), etc., with heat treatment and cyaniding ;
2. Alloy steels with 0·2% carbon, such as 15 NM (A4615), 20Kh (A5120), 20KhN (A3120), 12KhN3 (A3312), etc. ;
3. Steels with 0·25–0·35% carbon, such as 30Kh (A5130), with surface cementation ;
4. Steels of U.S. type A5140, with 1% copper, cast.

High chromo-silicon steels are used for tractor engine valves, e.g., SKh8 and SKh8M, with a carbon content of 0·35–0·50 :—

	Si	Cr	Mo
SKh8	2·0–3·0	8·0–9·5	—
SKh8M	2·0–3·0	8·0–9·5	0·2–0·4

Instrument steels include both plain carbon steels of the U series and also alloy steels, chiefly of the chromium type, including chromo-silicon and chromo-manganese. In some cases, as in the Kh12 and Kh12M type—as indicated in the mark—the chromium content is 11–13%, and the steels are subjected to special heat treatment, including annealing in oil or air at 975–1,030° C.

Metal working and stamping steels are also of some interest, and include the predominantly chromium types : 6KhNM, 5KhGM, 4KhS, 6KhS, 4KhVS, 7Kh3, etc. There are besides, several other special steels (about 27 marks in all) included in this class, such as 5KhNM, 3KhV8, KhG, Kh12, Kh12M. The three last are used for hot stampings, and are said to have deep tempering or annealing properties, and permit isothermic annealing of large section stampings.

High speed cutting steels are usually of the type RPh1 (R18 or 18–4–1), containing 0·7–0·8% carbon, 17·5–19% tungsten, 1·1–1·4% vanadium, 0·5% molybdenum, 3·75–4·5% chromium, up to 0·4% manganese, plus a little sulphur and phosphorus. Descriptive marks are not used in this class, but some of them have the class mark EI, thus :—

Mark	C	W	Mo	Cr	V
EI 184	0·8 –0·95	4·5	—	7–9	1–1·4
262	0·85–0·95	8·5–10	—	4–4·6	2–2·6
290	0·90	3	3	4	2
U.S.A.	0·75–0·9	5–6	3·5–5·5	3·5–5	1·25–1·79
U.S.A.	0·80–0·90	5–6	1·2–1·5	4·2–4·8	1·4–1·6

At a meeting of the Board of Vicker's, Ltd., held to-day, it was decided to recommend for approval at the annual general meeting, to be held on May 14th, 1948, a final dividend on the Ordinary Stock of 8½% actual, less income tax, making 12½% for the year ended December 31st, 1947 (same as 1946). Subject to such approval, payment will be made on May 15th, 1948.

Net profit of Vicker's, Ltd., for the year, after providing for taxation, etc., but before transfer to Sinking Fund (as below) is £1,225,238 (£1,076,224 in 1946). Certain Reserves and Provisions in the Accounts of Subsidiary Companies no longer required for the purposes for which they were created and amounting to £4,513,767 (nil 1946) were transferred to the Reserves of the parent company.

Reviews of Current Literature

The Plating of Zinc Alloy Die Castings

THIS excellently produced little manual worthily reflects upon the publications committee of the Zinc Alloy Die Casters' Association, headed by L. A. J. Lodder, B.Sc., A.R.C.S., of the Research Department of the Imperial Smelting Corporation Ltd. All aspects of the subject of electroplating zinc castings are covered in a logical sequence under clearly defined sections. A mass of factual information is presented neatly and concisely, accurately indexed for easy reference, without any irrelevant matter or superfluous wording, and efficiently edited.

The general aspects of the subject are confined to a useful but brief introduction, so that the text in five chapters can enter direct upon technicalities. This is achieved under five main headings, viz., production of castings for plating, the actual plating operation, maintenance of plating baths, tests and specifications, and the removal of plated coatings from die castings. With clear sectioning and sub-sectioning, this proves a very effective mode of presentation.

Under the heading of " Production of Castings for Plating," it is gratifying to note that the first requirement is " design for plating," and to see this so adequately tackled. All methods of preparatory polishing, including barrel treatments, are discussed, and the cleanliness of the polish is stressed. The subsequent cleanses, solvent, alkali and acid treatments, necessary for proper preparation for plating, are analysed in detail ; even the importance of attention to wash-waters with special reference to calcium-hardness is considered.

The chapter on " Plating " deals authoritatively with the primary coating, viz., copper or nickel, presenting the advantages and disadvantages, or merits and de-merits, of each practice, so that a reader is in no wise confused or biassed. Concisely recommended processes are given, but so are brief details from latest research and development. The thoroughness of the publication is evidenced by mention of a number of small but exceedingly important points, so often ignored by platers, e.g., a warning not to use air agitation for Rochelle copper electrolytes, but the advantages of mechanical agitation, and the need for a brief dip in dilute acid between alkaline copper plating and acid nickel plating. Attention is given to latest commercial processes such as the alkaline copper pyrophosphate electrolyte of the United Chromium Inc. Much detail is presented on nickel plating processes, and bright nickel plating is given very special attention. On this subject, a mass of tabulated information is included from the practices of three large American companies. The normal procedures for chromium plating (over nickel) and for direct chromium are cited. Practices for other platings, including silver and black nickel, and for combinations of enamelling and plating are included. Barrel plating is treated adequately in a separate section.

" Maintenance of Plating Baths " embraces the causes of changes in electrolyte composition, analytical and pH control, surface tension determinations, and contamination and removal of contaminants. Practical detail is given on chemical processes of purification, electrolytic methods, and filters and filtration.

Under the heading of tests, the several methods for determining the thickness of coating are discussed, and also adhesion tests. Recommendations for thicknesses of plating are given for various classes of work and service conditions, as well as values from A.S.T.M. specifications. The importance of adequate plating thickness is stressed, and it is indicated that the additional cost of producing an adequate coating is a very small percentage of the total production cost of the article.

The practical fact that it is not only necessary to apply a sound plated coating to a die casting, but also, upon occasion to remove it, is not overlooked. Suitable stripping methods are given with a warning that generally it is preferable to scrap the castings.

The success of plating processes is illustrated by photographs showing the complexity of shapes that can be satisfactorily processed. Finally, a chart is included giving full operating details for typical plating procedures.

The representation of modern authoritative work on the subject is evidenced by the 121 references quoted in the text ; these are summarised together at the end of the book, a commendable procedure.

One is tempted to predict that a sound answer to any question on the plating of zinc die-castings can be found in this book. Certainly, it is many years since so much factual information was so concisely presented in so few pages for so small a charge ! The authors are to be congratulated upon their effort, and ZADCA for enabling the book to be published.

Published by the Zinc Alloy Die Casters' Association (ZADCA), October, 1947. Distributors : Machinery Publishing Co. Ltd., National House, West Street, Brighton, 1. 132 pp., 14 illustrations, 7s. 6d. nett.

Aluminium and Aluminium Alloys in the Food Industry

The importance of aluminium in the food industry has increased steadily over many years, and it is now used extensively for plant, equipment, containers and wrapping materials. In planning further research with a view to extending the usefulness of the metal, the Low Temperature Research Station, D.S.I.R., has carried out a thorough survey of all the available information relating to the properties of aluminium and its alloys which might conceivably affect their corrodibility. This information, which was highly scattered and unco-ordinated, is given for the first time in this single comprehensive and critical report.

Aluminium possesses many desirable qualities which render it suitable as a material for use in contact with foods and beverages, and it is already well established in certain branches of the food industry, notably in Dairying and Brewing. The report should be of value to food technicians and to others interested in aluminium generally. The author's own experimental results are woven into the text.

The survey clearly shows that aluminium is inherently a very re-active metal, and that its resistance to corrosion is entirely due to the presence of a highly protective film of oxide on the surface. The protective properties of this film have been considered both in relation to particular conditions at the surface of the metal and to those in the solution with which it may be in contact, for it is known that corrosion can be greatly influenced not only by the structure and composition of the metal

at the surface, but also by the power of ionised substance in solution to penetrate, undermine or dissolve the film.

It was necessary to consider the action of simple aqueous solutions—e.g., acids, salts, inhibitors, etc., in order to gain an insight into the corrosion by complex substances like foods.

While the factors external to the metal are dealt with in great detail, the special problems relating to the metal itself—e.g., those encountered in marine engineering, are outside the scope of the report. There is no evidence that any properties injurious to health are imparted to foods which have been cooked or held in aluminium vessels, and aluminium neither accelerated the destruction of vitamins during cooking nor catalyses the oxidation and rancidity of fats. It also has no effect on yeast fermentation.

The effect of food products on aluminium is considered in great detail, and the practical information on the aluminium can and other aluminium packing materials should be of considerable value to the food industry.

The report is divided into four parts. The first part considers briefly the metal and the surface film in relation to the different types of corrosion which may develop. The second part gives a detailed account of the corrosion by aqueous solutions, while the third part covers thoroughly the corrosion by different types of food products and beverages. The last part discussed the various methods of protecting aluminium, viz., by oxide coatings, metallic coatings, cathodic protection, paints and lacquers.

Food Investigation Special Report No. 50, by the Department of Scientific and Industrial Research. Published by H.M. Stationery Office, 154 pp., 17 illustrations, price 3s. net, by post 3s. 4d.

Copper Pipes Underground

The use of copper tube underground and the revision of out-of-date bye-laws in certain areas which have the effect of banning such use should be greatly stimulated by this publication. Superseding a previous booklet, "The Resistance of Copper to Soil Corrosion," this new publication contains much more extensive data, acquired by means of field tests, and further records of practical experience, made available since the issue of the earlier booklet. The effect of the new with the old information is to provide striking testimony as to the superior resistance of copper to soil corrosion.

In the great majority of soils, it is stated, copper has an almost unlimited life, while in some of these soils other materials commonly employed are eaten through in a few years. Copper pipes need protection only in a few exceptional types of soils, in which pipes of other materials would be at least as liable to attack.

Commenting on the field tests carried out by the British Non-Ferrous Metals Research Association on copper and lead and by the U.S. National Bureau of Standards on copper, lead, steel and cast iron, the publication shows that copper proved to be the most satisfactory material.

Evidence of resistance to corrosion in service in this country of copper pipes underground includes the fact that it is nearly 22 years since experiments were first carried out by the Nairn Gas Light Company, with such satisfactory results that copper has been adopted locally for all gas services employing $\frac{3}{4}$-2-in. diameter light-gauge tubing. No internal or external corrosion trouble

has been experienced. Various services have been opened at intervals, test pieces cut out and found to be as good as when they were laid.

For underground water pipes, copper has been used since 1919 in Dundee, where, as in some other areas, it is now unusual for any other material to be used for the service pipes between stopcock and house. In Manchester, the practice of employing 1-in. 18 s.w.g. copper pipes as subsidiary mains, feeding short streets or *cul-de-sacs*, has been employed for about 22 or 23 years. Many miles of copper tube have been used, and there has been no trouble whatever with soil corrosion.

"Copper Underground: Its Resistance to Soil Corrosion," published by Copper Development Association, Kendals Hall, Radlett, Herts. Issued free to applicants having genuine interest in the subject.

Chemical and Electroplated Finishes
The Protective Treatment of Metals

In this book, the author set out to present a broad survey of finishes that are commercially applied to metals from aqueous solutions with or without the use of electric current. To achieve this within a reasonable compass, he has eliminated all discursive writing, references to obsolete processes or to those unlikely to be established in the near future, fundamental theory that can be obtained from text books, and mention of proprietary products unless some indication of composition or principle of process could be given. In this, he has fully succeeded and the book should prove an unqualified success in providing a factual survey of a field that is by no means overburdened with comprehensive treatises.

The corrosion of the common metals of engineering is dealt with briefly but in a sound useful manner. Descaling and pickling processes are comprehensively treated, attention being given to hydrogen embrittlement, the use of inhibitors and wetting agents and the role of chromic acid in nitric/sulphuric acid dips. It is disappointing not to find reference under the ferrous metals to the sodium hydride process, and under the copper rich metals to sulphuric acid/dichromate or ferric sulphate pickles. Polishing covers all methods, manual, automatic and barrel, the wheels and the compounds, and electropolishing. Degreasing and cleaning embraces plant, process and materials for solvent, aqueous alkali and electrolytic methods. The value of wetting agents in the aqueous solution is demonstrated.

A section is devoted to metal colouring for decorative and light duty finishes. Under this is justifiably included at some length the phosphate treatment of iron and steel and of zinc coatings. A summary of processes for giving various colours on all metals, steels, coppers, brasses, cadmium, zinc and aluminium is given.

With respect to electroplating, plant and equipment is dealt with broadly: tanks, linings, pumps, filters, heaters, generators, rectifiers, etc., etc. Under general principles of plating, it is felt that more fundamental attention could have been given to the significance of throwing power and its measurement.

Precious metal plating is confined to rhodium, gold and silver, which represents normal general practice; a little more information on bright silverplating and on tarnish preventatives would have been useful. Nickel plating is considered at length and very thoroughly,

including the application to zinc castings and bright nickel techniques, and the use of wetting agents. Under chromium, are included the decorative and wear resisting types of coating, and mention is made of porous chromium platings that are said to have greater wear-resistance because they retain oil.

Copper is considered in relation to an undercoating for nickel as a basis for coloured bronze finishes, as a stop-off medium for case-hardening, and in electro-forming and the production of printing plates. The Rochelle salt type of bath is fully discussed, and information given upon pyrophosphate electrolytes, copper sulphamate solutions and the American high-speed cyanide processes. The fluo-borate method is not given. Brass plating is also briefly covered in this section.

The continuous tin plating of steel strip and the filming of tin plate are dealt with briefly. In the same section, tinalloy plating is presented in a brief manner, i.e., "speculum" (tin-copper) and tin-zinc alloys.

Cadmium plating is given the position it deserves and the improvement imparted by chromic passivation is noted. A little more guidance on the best practice with respect to dull or bright deposits, current conditions, etc., would have been welcomed.

The section on zinc is confined to the orthodox cyanide, zincate and sulphate electrolytes, to the mercury modified bath, bright zinc, and electro-galvanising of wire, and to chromate passivation. As the least expensive of electro-platings, and the widest applied for protecting steel, more details could have been given with advantage. The fluo-borate electrolyte is not given. Useful data are presented for lead plating.

To the finishing of aluminium and magnesium light alloys is allocated a separate section. The principal anodising processes are ably dealt with, including dyeing and sealing, and special processes for reflectors. The American process for anodising and dyeing in one bath is not mentioned. Chemical immersion processes for aluminium are briefly described, i.e., M.B.V. and Pylumin ; the chrome-sulphuric pickle is a notable omission. Electro-plating processes are aptly but briefly covered. Magnesium alloys are very tersely dealt with on the basis of chromate immersion and anodic treatments.

The author has obviously adopted the commendable principle of providing full working data in a clear scientific manner on every main process cited and of including recommendations appertaining to really suitable plant, troubles, etc. It is considered that this volume may well be the forerunner and basis of a more comprehensive treatise, perhaps split into two or more parts, particularly as this field of metallurgy is very much in its infancy, and finishes on zinc, aluminium and magnesium are assuming primary importance. It is to be hoped that the author will be enabled to continue the good work.

By H. Silman, B.Sc., F.R.I.C., A.M.I.Chem.E., with foreword by H. Moore, C.B.E., D.Sc., published by Chapman & Hall, Ltd., 1948, 414 pp., 131 illustrations, 30/- nett.

Exhibition of Scientific Instruments and Apparatus

THE important part that scientific instruments play in research is generally recognised, but their value in a great many operations, in practically all industries, is not fully appreciated. Many instruments that were formerly confined to the laboratory have been developed for workshop use and in many cases have become indispensable in the control of operations. Those who had the opportunity to visit the exhibition of scientific instruments and apparatus recently held at the Imperial College of Science and Technology in London, under the auspices of the Physical Society, would see some of the remarkable developments in this field achieved in recent years. For those unable to visit the exhibition a brief reference to some of these developments will be of interest.

Especially interesting is the wide field of instrumentation in the iron and steel industry, which was demonstrated by the British Iron and Steel Research Association. At the iron-making stage, for instance, an immersion pyrometer is used to measure the temperature of molten iron from the Association's experimental blast furnace, where the flow of iron is over within 15 secs. Radiation from the end of the silica sheath immersed in the liquid is fixed upon a high speed thermophile.

At the steelmaking stage a remote indicating roof pressure meter was shown for open hearth furnaces. The differential pressure between the atmosphere within and outside the furnace being registered by an electrical null balance technique of measurement which readily lends itself to remote indication of the readings in the form of an electrical signal. The differential pressure development on a free diaphragm is automatically balanced by the force set up on a current carrying coil moving in a uniform magnetic field. The current in this coil at the balanced condition is a measure of the differential pressure applied. Also applicable to the steelmaking stage is a carbon tube furnace which, by means of a carbon tube directly heated provides a black body source 2 in. diameter for the calibration of total radiation pyrometers. The temperature of the furnace may be varied from 1,000–1,750° C., and thus affords a means of calibrating steelworks pyrometers *in situ*. Such a pyrometer is the mirror-type total radiation pyrometer which, because of its compact size can be mounted on the front wall of an open hearth furnace. It is based on the ordinary thermocouple principle, but embodies two thermocouples made of well-known alloys, and the cold junctions are located in the pyrometer casing, which is water-cooled, so that the variation in the ambient temperature is a minimum.

The sulphur dioxide recorder shown also applies to the steelmaking stage, and is used for recording the SO_2 content of fuel and flue gases. In a steelworks, requirements of very high sensitivity and fast response have to endure through long unattended periods in severe conditions. This new design of SO_2 recorder meets these demands by converting SO_2 from a continuous sample into sulphuric acid in a countercurrent scrubbing tower. The electrical conductivity of the reagent is measured

before and after absorption and the difference used to operate a recording millivoltmeter.

Instrumentation at processing stages is exemplified by a wiredrawing profilometer, and by a portable roll force meter. This last has been developed by B.I.S.R.A's rolling mill team at Sheffield to record at a distance the vertical force between the rolls during the passage of the stock through the mill. The instrument shown was designed to measure loads up to 50 tons, and is readily transportable to a works, where it can be installed in the course of an hour or so. These meters are being developed for loads up to 250 tons and more.

Much interest was shown in Metropolitan-Vickers new electron microscope, type EM3, which is the successor of the EM2 series. It employs a three-lens image-forming system ; this reduces the overall size of the microscope and increases the range of magnification that can be obtained. This feature, combined with a new lens design allowing the coil windings to be external to the vacuum, results in the pumped volume being considerably reduced, so that the pumping-down time is approximately 2 minutes, and no airlocks for specimen or camera are employed. The movement of the mechanical stage allows the whole of the specimen to be scanned and also provides for stereoscopic work

A new version of the " Universal " type of crack detector in which the specimen is magnetised both transversely and longitudinally by means of D.C. flux and alternating current, demonstrated by Metropolitan-Vickers is versatile and can be adjusted to accommodate components of any shape or size up to 48 inches long and 8 inches diameter. The equipment has the advantage of being floor mounted.

Two pieces of laboratory measuring equipment of considerable scientific interest were shown by the General Electric Co., Ltd. One was a vibrating quartz-fibre pressure-gauge, to which attention has lately been redirected for its usefulness in investigating internal conditions in gas-filled valves. It was used to measure pressure changes inside a sealed-off hydrogen thyratron, a purpose for which it is particularly suitable. The other equipment was an apparatus designed to allow accurate measurement of the small changes in the density, as for example, that which occurs when glass is kept for a long period at temperatures in the range from $400°$–$500° C$. A flotation method is used in which distilled water is the flotation liquid and the difference in density between the liquid and the solid is compensated by means of a float.

It is noteworthy also that the Vernouil technique of manufacturing sapphire " boule " has been modified so that sapphire rod can now be produced. This has the great advantage that, since it can be made in suitable diameters, its use greatly reduces the labour of making circular jewel-blanks for the low-friction bearings required in electrical and other accurate measuring instruments. Samples of rod were exhibited by the General Electric Co.

Among the many instruments exhibited by the B.T.H. Co. were some exhibits illustrating and describing new glasses which have been developed for the special purpose of acting as a " solder " and enabling, for example, glass, metal and mica to be soldered to glass. The physical characteristics that a solder glass must possess are a coefficient of expansion comparable with that of the articles being soldered, and a suitable viscosity/temperature relationship. If two pieces of glass tubing are soldered together, for example, the solder glass must have the same coefficient of expansion as the main glass to prevent cracking under thermal stresses, but have a very much lower viscosity at the temperature of soldering, so that it will readily flow and thus make a good joint. In addition, the chemical resistant and weathering properties of the glass must be equal to those of standard glasses.

The exhibition proved both interesting and informative and indicated the progress being made in the development of scientific apparatus, particularly the instruments and apparatus which have emerged from the experimental stage to that of practical application.

Iron and Steel Institute

THE Annual General Meeting of the above Institute will be held on May 5th-6th, 1948, in the Lecture Hall of the Royal Institution of Chartered Surveyors, 12, Great George Street, London, S.W.1. At the initial meeting the Bessemer Gold Medal for 1948 will be presented to Mr. W. J. Dawson, C.B.E., in recognition of his contributions to the development of steel castings and to the production of alloy and heat-resisting steels : the second Sir Robert Hadfield Medal for 1948 to Mr. A. Preece, in recognition of his researches on the scaling and on the overheating and burning of steel ; and the Williams' Prize for 1947 to Mr. R. Fowler, for his paper on " Blowing out a Blast-Furnace." These presentations will be made by the Retiring President, Dr. C. H. Desch, F.R.S., who will then be followed in the Chair by Sir Andrew McCance, D.Sc., F.R.S., who will deliver his Presidential Address. Following this address, three papers will be presented for discussion at this morning session. There will be joint discussion on two papers dealing with " Construction and Repair of Open-Hearth Furnaces," and " The Design of Open-Hearth Gas-Ports," respectively, and the third paper will deal with Installation and Use of Instruments on Open-Hearth Melting Furnaces.

At the afternoon session on May 5th, four papers will be presented ; there will be joint discussion on two papers entitled : " The Production of Nodular Graphite Structures in Cast Irons," and, " The Carbides in Iron–Carbon–Silicon Alloys and Cast Irons " ; and also on a further two papers entitled : " Abnormal Creep in Carbon Steels," and, " The Creep Properties of Molybdenum, Chromium–Molybdenum, and Molybdinium–Vanadium Steels." At 8-30 p.m. on the same date, Professor Robert F. Mehl, of the Carnegie Institute of Technology, Pittsburgh, Pa., U.S.A., will present the Third Hatfield Memorial Lecture, the subject being : " The Decomposition of Austenite by Nucleation and Growth Processes."

The morning session of May 6th will be devoted to joint discussions ; one on three papers entitled : " A Micro-Examination of Eight Steels for the Inclusions Sub-Committee " ; " The Study of Segregations and Inclusions in Steel by Micro-Radiography " ; and, " Some Thermodynamical Aspects of the Formation of Inclusions in Mild Steel Weld Metal." A second joint discussion will follow the presentation of two papers entitled " A Comparison of Moulds of Standard Composition and of Approximately Ingot Mould Sub-Committee Composition " ; and, " Mould-Weight/Ingot-Weight Ratio and its Relation to Mould Consumption."

Staff Changes and Appointments

MR. N. W. READ, B.Sc., has left Messrs. David Brown and Sons Ltd., Huddersfield, to become Technical Officer (Metallurgist), in the Metallurgical Section, Engineering Dept., Imperial Chemical Industries Ltd., Dyestuffs Division, Hexagon House, Blackley, Manchester, 9.

MR. J. M. REID, B.Sc., has been transferred from the Research Dept., Imperial Chemical Industries Ltd., Metals Division, Witton, to undertake development work at the Landore, Swansea, works of the Company.

MR. E. D. HARRY has resigned his post as metallurgist with the Workington Iron and Steel Co. Ltd., and has now taken up an appointment as a metallurgist with the Steel Company of Wales Ltd., at Newport, Mon.

MR. J. E. MILLER has taken up the position of London Manager of the Chesterfield Tube Co. Ltd., with offices at The Adelphi, Strand, London, W.C.2.

MR. FRED MILLS, recently resident engineer to the Steel Company of Wales Ltd., has retired after 44 years' association with the iron and steel industry. He served his apprenticeship with Messrs. Baldwins Ltd., beginning in 1904, and was chief engineer from 1914 until 1944 During this period he was responsible for the layout of the Margam iron and steel works, giving particular attention to the design and erection of the steelworks section, and new plant at Gowerton, Wildon and Panteg.

MR. HOWARD E. N. STONE has left the Mond Nickel Co. Ltd., Birmingham ; he has joined the British Iron and Steel Research Association, and is stationed at the National Physical Laboratory, Teddington.

MR. WILLIAM UDALL has been appointed chief engineer of the Brightside Foundry and Engineering Co. Ltd., Sheffield.

MR. P. F. JONES and MR. C. N. SILVERSIDES have been appointed divisional engineers of the equipment division of Specialloid Limited.

MR. R. H. S. TURNER, M.A., has been appointed superintendent, plant department, Metropolitan–Vickers Electrical Co. Ltd., in succession to the late Mr. F. A. Pucknell.

MR. D. C. HENDRY has been appointed general manager and chief engineer of the planning and reconstruction department of the Corby works of Stewarts and Lloyds Ltd. MR. J. GLENN has been made general manager of the iron and steel works.

MR. T. A. MCKENNA has been appointed managing director of the Staveley Coal and Iron Co. Ltd. in succession to the late Mr. H. H. Berresford. MR. S. N. TURNER has succeeded Mr. McKenna as deputy managing director.

MR. A. F. ECA DA SILVA, Rua Candido Mendes 105—apto 501, Rio de Janeiro, has been appointed resident sales engineer in Brazil of Specialloid Ltd. Mr. Eca, who has had considerable experience in the Brazilian motor trade, will be responsible for the interests in that country of Specialloid Limited and other manufacturers for whom they act as export agents to Brazil. These include the Glacier Metal Co. Limited, Harold Andrew Grinding Company, the Steel-Tite Piston Ring Co. Limited and Prince (Kingston) Engineers Limited.

MR. J. SAVAGE has been appointed Deputy Head of the Physics Department of the British Iron and Steel Research Association, in addition to his duties as Head of the General Physics Section. Mr. Savage will take over certain administrative duties of the Department.

MR. D. L. DAVIES has left the United Steel Companies Ltd., to take up an appointment with Richard Thomas and Baldwins, Ltd., Panteg Works, Griffithstown, near Pontypool, Mon.

MR. JOHN O. EDWARDS is relinquishing his position with the British Aluminium Co. Ltd. to take up an appointment in Ottawa with the Metallurgy Division of the Bureau of Mines.

MR. J. H. M. REID has been transferred from the Research Department, Witton, Birmingham, to the Landore Works, Swansea, of the Imperial Chemical Industries, Ltd., Metals Division.

MR. A. H. DIXON is going to South Africa on behalf of Messrs. Ashmore, Benson Pease and Co. Ltd. His address will be Ashmore, Benson Pease and Co. Africa (Pty.), Ltd., P.O. Box 8608, 901–905, Jubilee House, 15, Simmonds Street, Johannesburg, South Africa.

MR. GERALD E. TANNER has left the Appleby-Frodingham Steel Company, where he held the position of assistant plate-mill manager, to take up an appointment as manager of the 32-in. section mill at the Cargo Fleet Iron Co. Ltd., Middlesbrough.

DR. ROBERT J. ANDERSON, Met.E., has resumed his consulting engineering practice, specialising in the metallurgy of aluminium and magnesium. Pending his removal to a permanent location, his address is 125 N. Portage Path, Akron 3, Ohio, U.S.A.

MR. P. T. GILBERT, B.Sc., A.R.I.C., has been appointed head of the Corrosion Section of the British Non-Ferrous Metals Research Association.

MR. ALAN R. BAILEY, B.Sc., A.I.M., has been appointed Senior Lecturer in Metallurgy at the Constantine Technical College, Middlesbrough.

MR. R. J. L. EBORALL has been appointed head of the General Metallurgy Section of the British Non-Ferrous Metals Research Association.

MR. A. HAZELL, B.Sc., has left the die-casting department of the B.T.H. Co., Birmingham, and has joined the staff of Wm. Mills Ltd., Wednesbury. He will be responsible for the development of a pressure casting section.

PROFESSOR C. E. PEARSON, M.Met., has resigned from the William Cochrane Chair in Metallurgy at King's College, University of Durham, to take up a post with Durham Chemicals Ltd., Birtley, Co. Durham.

DR. MORRIS REED, Ph.D., M.Sc., M.I.E.E., has been appointed chief radio engineer of the Mitcham Works of Philips Electrical Ltd. He will be in charge of all engineering activities relating to radio and television receivers and allied apparatus.

Errata

The footnotes 7, 9 and 13, on page 271 of March, 1948, issue should be :—

7 " Methods of Chemical Analysis of Metals," Amer. Soc. for Testing Materials, 1946.
9 " Organic Reagents for Metals and for Certain Acid Radicles," Hopkin & Williams, Ltd., 1943, page 141.
14 Pigott, E. C., " Micro-chemical Analysis—Application to Iron and Steel," *Iron and Steel*, 1943, 17, 140.

A Discussion on Routine Chemical Methods for the Analysis of Niobium and Tantalum Bearing 18/8 Steels[*]

By B. Rogers, A.I.M.

Research Dept., Murex Welding Processes, Ltd.

Subjects discussed include :—(a) The essential chemical principles involved in the determination of niobium, tantalum and tungsten in steel. (b) T. R. Cunningham's procedure for the determination of niobium and tantalum in 18/8 Nb-Ta steels ; and its application to the analysis of these steels when 0–0·6% tungsten is present with molybdenum in varying amounts, and up to 0·1% titanium. (c) The analysis of niobium, tantalum and tungsten steels when the amount of tungsten is greater than 0·6% W. (d) The determination of any of the additional alloying elements cobalt, copper, tin and selenium, which do not normally interfere with the determinations discussed above.

Introduction

THE determination of niobium and tantalum in 18/8 Nb–Ta steels involves the separation of the acid group [1], which includes niobium, tantalum, silicon, tungsten, tin and vanadium. Usually the steel is dissolved in aqua regia, and the solution is evaporated with sulphuric or perchloric acids ; or, a baking procedure is used as for the determination of tungsten in steel.

W. R. Schoeller states that niobium and tantalum behave chemically in a similar manner to tungsten and silica.[2] In procedures used for the determination of niobium and tantalum in 18/8 Nb–Ta steels a solution of the steel is obtained which will permit of the niobium and tantalum being finally hydrolysed by boiling, or precipitated by tannin or cupferron and weighed as the pentoxides. Some tungsten is precipitated using T. R. Cunningham's[3] and E. J. Harpham's procedures,[4] and initially applied cupferron procedures.

Baking procedures are used to collect quantitatively all the niobium, tantalum and tungsten present in the steel as mixed earth acids. The former mixed earth acids must be separated from tungsten acid by various procedures, which are discussed later, before separating niobium from tantalum prior to the quantitative determination of these elements.

Separation of the Acid Group

G. F. Lundell[1] has outlined what happens when hydrochloric, sulphuric, perchloric or nitric acids are used as agents of dehydration. Occlusion or co-precipitation of various elements is likely to occur if the precipitate is hydrolysed without using a baking procedure or following a baking procedure.

Treating the acids in sequence, these points are relevant to this discussion :—

(a) *Hydrochloric acid.*—Silicon, carbon and boron are the main interfering elements. F. Ibbotson[5] stated that a 20% solution of hydrochloric acid may be used for separating molybdenum from tungsten.

(b) *Sulphuric acid.*—Earth acids tend to occlude molybdenum, iron, chromium, tin, aluminium and boron.

(c) *Perchloric acid.*—Allows vanadium, tin, manganese, molybdenum, phosphorus, carbon, fluorine and potassium to be partially occluded by earth acids. Used alone, this reagent is not so useful as hydrochloric acid.

(d) *Nitric acid.*—Vanadium, molybdenum, tin and boron are occluded by earth acids. There is scope for using nitric acid as a collector of such elements, it is suggested, for some analyses.

(e) It may be added that *phosphoric acid* is not of obvious value for these schemes of analysis as, when used in modifying T. R. Cunningham's procedure for the determination of niobium, it results in a low weight of the final pentoxide residue. Again F. E. Eborall[6] found that phosphoric acid tends to form vanado-phospho-tungstates in the solution of high-speed steels.

Discussion of T. R. Cunningham's Procedure for the Determination of Tantalum and Niobium (approx. 0·6% present) in 18/8 Mo Steels

There may be present up to 0·1% Ti ; if otherwise a cupferron procedure is used. This excellent procedure is the best and most direct one for steel analysis. It will be seen to conform to the best relevant theoretical principles discussed above. Perchloric acid is used as the dehydrating agent ; and aqua regia as the initial solvent, as it offers a speedier solution than does hydrochloric acid used alone. The nitric acid is removed from the solution by the fuming operation with perchloric acid (60–70% $HClO_4$). This operation is quite safe as there remain only a little refractory carbides, probably carbides of niobium and tantalum. A good draught is advisable and the use of perchloric acid under these conditions here has never given any trouble. After dehydration organic matter must be carefully avoided. Even a duster will tend to "spark" when removing the covered beaker from the hot plate. Hydrochloric acid is then introduced—i.e., good solvents (and perchloric acid is a good solvent for refractory oxides, inclusions and carbides), are followed by the most suitable acid which may

* Received, October 21, 1947.
1 Lundell, G. F., and Hoffman, J. I., "Outlines of Methods of Chemical Analysis," Ch. 7.
2 Schoeller, W. R., "The Analysis of Ores and Minerals of Rarer Elements," 1940, p. 161.
3 Cunningham, T. R., "The Determination of Tantalum and Niobium in 18/8 Steels," *Iron Age*, May 15th, 1938, **5**, 255.
4 Harpham, E. J., "The Chemical Determination of Tantalum and Niobium in Tungsten-bearing Heat-resisting Steel," *Metallurgia*, March, 1946.
5 Ibbotson, F., "The Chemical Analysis of Steelworks Material, 1918, **135**, 146.

6 Eborall, F. E., "A Compound Method for the Absorptiometric Analysis of High and Super-high-speed Steels, *Metallurgia*, Dec., 1946, p. 104.

be used for a solution from which to separate niobium from iron. Sulphurous acid is added to the diluted solution and boiling then serves to complete the reduction of the chromates formed by peroxidation. In this procedure iron, chromium, molybdenum and manganese are thus separated from niobium pentacid which is hydrolysed by boiling for 5 minutes ; pulp is used to help to collect the precipitate. Silica is removed from the ignited residue by the usual sulphuric acid - hydrofluoric acid treatment. Carbon is removed during the various operations, including ignition. It is interesting to note that no significant amounts, in routine work, of nickel and chromium have been found to be insoluble in sulphuric acid solutions of niobium bearing 18/8 steels used for nickel and chromium determinations which were oxidised by nitric acid when the dimethylglyoxime and the Vignal Procedures were used. Molybdenum, if present in large amounts in the steel, may possibly be present in the carbides ; but in aqua regia solutions the loss is not significant. Work is proceeding on this point in connection with colorimetric schemes combined with chemical methods.

The removal of silica from the residual pentoxides of niobium and tantalum involves several major points. Niobium and tantalum pentoxides are soluble in hot strong hydrofluoric acid[7]. No loss of niobium is incurred in this operation, but trouble is encountered if all the hydrofluoric acid is not volatilised, leading to low figures ; or if the evaporation is allowed to go too far (below 2 mls. volume). Molybdenum (blue) oxides will, if present, be partially occluded in the residue ; and the salts of aluminium, chromium, nickel and iron may also be present. It is always good practice to add 2 mls. of perchloric acid to the hydrofluoric-sulphuric acid solution *initially*. This saves time as trouble may be otherwise encountered without it. (No trouble is met when it is used and a third precipitation is hereby avoided). Two precipitations in hydrochloric acid solution, the second in 2% acid, yield a pure white pentoxide, finally—i.e., upon ignition of the filtered and washed precipitate. Potassium bisulphate fusions are avoided in this procedure (which G. F. Lundell permits in his procedure[8] and so potassium is possibly occluded, as in some other procedures, by the pentoxides of niobium and tantalum). Alkali fluorides[9] demand the presence of sulphuric acid in the operation for the removal of silica from niobium pentoxide, etc.

In practice, some difficulty has been met in filtering colloidal hydrolysed precipitates. Routine technique giving satisfaction here for years is based upon the use of a Buchner funnel, taking a 7 cms. disc of No. 42 Whatman's filter paper, inserted as usual, in the funnel, followed by three pulped discs of 15 cms. Whatman's No. 42, ashless filter papers which are used as a filter pad, being placed on top of the disc and lightly pressed down. The discs are counted and a blank operation is carried out for accurate work, to determine the ash of the pulp. *Shallow platinum dishes* (36 gm.) are then a very convenient size for the ignition and fuming operations. They save much time. It is not difficult to obtain agreement between different operators to ± 0·02% Nb using this procedure, in routine.

Titanium is usually present in very small amounts in

18/8 Ni steels and may be determined colorimetrically upon the bisulphate solution of the ignited residue of the pentoxides using hydrogen peroxide as the reagent for forming the colour. The colour may be compared visually against a previously prepared series of standard colour solutions or by a Spekker procedure, or, by the ordinary dilution method in which a solution of titanium sulphate is added to the reagent blank solution until the colours are matched.

Tantalum, if present, remains quantitatively with the niobium and is determined by W. R. Schoeller's well-known procedure,[10] or as used by T. R. Cunningham.[3]

Tin, if present, is practically insoluble[11] in potassium bisulphate fusions and may be filtered off. A direct distillation procedure[12] is in satisfactory use here for the determination of tin in 18/8 niobium steels. Tungsten is determined by G. S. Smith's procedure[13] involving, as used by W. R. Schoeller,[14] grinding the weighed residue and taking 0·01 gr. of the mixed oxides and fusing this with sodium carbonate. The sodium tungstate solution is treated with stannous chloride solution in hydrochloric acid solution to give a yellow colour. Only small amounts of tungsten may be determined in this way.

Determination of Niobium, Tantalum and Tungsten in Heat-resisting Steels

The preliminary baking procedure.—From the above considerations and from specialised experience, it is, therefore, best to separate tungsten from steel, using hydrochloric acid only, wherever possible, and adding nitric acid in drops, at intervals of a few minutes ; baking only lightly and repeating the operation for 18/8 steels.[15] If baked " hard," bulky residues, high in content of iron, will be obtained owing to the formation of basic iron compounds.

Extraction of the baked residue with hydrochloric acid should be followed by boiling the extract down to 15 mls. total volume, followed by a dilution operation with 200 mls. of 5% hydrochloric acid and a settling period of several hours or overnight. For complete separation of tungstic acid cinchonine is of value. If niobium is present, cinchonine will help to collect the last traces of this element. Sodium thiosulphate and pulp have been used to assist in coagulation of the latter but call for a boiling operation of several minutes duration ; and to be effective in this connection, some time is required in which the hydrated earth acids may settle out of the solution.

If tungsten is absent from the steel, the above procedure may be used—i.e., iron is then separated by an ammoniacal tartrate-sulphide separation, preferably preceded by a hydrolysis stage as in T. R. Cunningham's procedure. If the hydrolysis stage is omitted discoloured residues may be obtained. Niobium may be occluded by iron sulphide precipitates.

Methods of separating tungsten from mixed earth acids.— Although dehydration procedures have been discussed several other points are involved in the subsequent choice of suitable procedures, mostly based upon an alkaline treatment of the mixed oxides obtained by baking the initial solution of the steel, ignition, etc.

7 Schoeller, W. R., " The Analysis of Ores and Minerals of Rarer Elements," 1940, p. 146.
8 Lundell, G. F., Hoffman, J. I., and Bright, H. A., " The Chemical Analyses of Iron and Steel," 1931, p. 365.
9 Schoeller, W. R., " The Chemical Analysis of Tantalum and Niobium," 1937, p. 16.

10 *Ibid*, p. 122.
11 *Ibid*, p. 53.
12 Baker, L., Miller, M., and Stevens Gibbs, R., " The Determination of Tin in Plain and 18/8 Columbium Steel," *Ind. Eng. Chem. Anal. Ed.*, April, 1944, **16**, 269–271.
13 Smith, G. S., " The Colorimetric Determination of Tungsten," *Ind. Chemist*, 1945 (244), 250–252.
14 Schoeller, W. R., " The Chemical Analysis of Tantalum and Niobium," 1937, p. 153.
15 Private Communication.

Tungsten must be separated *initially* from tantalum and niobium, states W. R. Schoeller[16], before separating the latter elements from each other. His methods are worked out in detail for mineral analyses. The application of such technique to steel analyses is not straightforward and *there seems to be a gap between the two specialised groups of workers. Collaboration is indicated as much time is lost in developing procedures.* Again, in tannin precipitations niobium induces the precipitation of tungsten more than tantalum does and the reverse is true for cupferron precipitations. Cupferron is valuable, therefore, for niobium determinations when tungsten is present in the solution. When the separation of tungsten from iron and zirconium only is involved the methods based upon carbonate, hydroxide or peroxide fusions may be used;[17] but when niobium and tantalum are present with tungsten, the application of these alkaline separations must be considered with regard to the influence of the niobium and tantalum present in solution or in residues. The following notes should be of assistance:—

1. Methods based upon ammonium carbonate and ammonia separations, used by W. Scott[18] and Johnson[19] are useful routine procedures and work fairly well. "Ammonia separations of tungsten from niobium are wrong in principle," Schoeller states,[20] but the point is not always significant in routine practice. In such treatments of similar residues or precipitates, as colloidal precipitates tend to pass through the filter paper usually used, in subsequent operations the writer has found it useful to add a little iron to the filtered solution, then to boil the solution and make an ammonia separation. (Colloidal titanium precipitates also respond to this treatment). Potassium carbonate should be used in Johnson's method (not as in the text).

Iron is also used to collect tungsten in small quantities.[21] Tin and niobium are collected by Lundell in this manner (without iron) following his digestion procedure for tungsten.[22] Tannin and cinchonine, if used, render this operation unnecessary if tungsten acid solutions are baked and treated with these reagents and the usual technique is applied in order to complete the operations.

Pulp may be used to collect tungsten acid but, if used in this manner, it is not so effective as cinchonine, it is found here. Perchloric acid cannot be used with cinchonine as it were too dangerous to do so even if it were a useful combination.

2. (*a*) Alkaline digestion with a solution of caustic soda of filtered and *wet*, unignited precipitates of tantalic, columbic and tungstic acids has been used here, with mixed success. Colloidal troubles occurred during filtering operations using a Buchner funnel and pulp. Thorough washing of the precipitate with a dilute (1%) soda solution is followed by a reprecipitation of the soda insoluble group (which is again washed as before) and the precipitate may then be redissolved in order to determine niobium :—

   (i) Using T. R. Cunningham's procedure, as iron is thereby effectively removed from the solution.

or (ii) By a tannin procedure in one precipitation[23] as

used here for the determination of titanium in rutile and ilmenite, and in residues high in content of iron. Two precipitations are often avoided by the use of empirical factors.

2. (*b*) Digestion of the solution of mixed earth acids with excess caustic soda—i.e., group 3 precipitates containing tungsten and columbium, as in G. F. Lundell's umpire procedure for the determination of niobium.

3. (*a*) Such partial separations of iron, yielding a precipitate containing all the niobium and tantalum, whether made by ammonia[24] or preferably by the bicarbonate[25] procedure of G. F. Lundell are not so easily applied to 18/8 steels. In the former case, the colour of the solution makes the separation a difficult one and the modern modifications, using pyridine[26] might facilitate this operation but have not yet been tried here. The solubility of the Ta-Ni-W-Co 18/8 steels in sulphuric acid is not complete for the bicarbonate procedure to be applied directly ; but, by taking an aqua regia solution of the steel to fumes with sulphuric acid, digesting any insoluble sulphates with caustic soda followed by reacidification with acid (preferably hydrochloric acid) it might be usefully applied. Or from the sulphuric acid solution, insoluble niobium and molybdenum carbides may be filtered off, ignited, fused with potassium bisulphate and the warm, filtered, extract of the fusion in sulphuric acid and water may be added with a reducing agent to the main solution. Digestion procedures involving fuming with sulphuric acid to destroy carbides may need the above-mentioned soda treatment. A cupferron procedure may then be used, with a tannin[27] separation of niobium and titanium from iron. This procedure has yielded excellent agreement with ether procedures[28] here on mineral analyses.

3. (*b*) Cupferron may be used initially to precipitate niobium, tantalum and titanium but unfortunately, some tungsten, if present, is occluded by the former group of earth acids. Tungsten will have to be separated prior to cupferron and tannin procedures. Sulphide precipitations require the examination of the residue for occluded earth acids, and the method becomes over elaborate.

4. (*a*) In practice, in one procedure[29] involving a potassium carbonate fusion of the residue of the mixed earth acids finely divided iron is not easily separated in the manner indicated—i.e., using a filter paper with pulp in the apex of the funnel. Repeated fusions of the residual oxides obtained by a baking operation are essential and are followed by the magnesium sulphate procedure for separating tungsten from niobium.[30] Discoloured residues are obtained if iron is not fully separated or if basic iron compounds are allowed to form in the baking stage. By following the magnesium sulphate procedure earth acids and complex mixtures of all the earths are separated from tungstic acid; and small amounts of earth acids in the tungstic acid precipitate are collected by a sodium hydroxide fusion of the ignited residue.[31]

16 Schoeller, W. R., " The Chemical Analysis of Tantalum and Niobium," 1937, p. 86.
17 Lundell, G. F., Hoffman, J. I., and Bright, H. A., " The Chemical Analyses of Iron and Steel," 1931, p. 327.
18 Scott, W. D., " Standard Methods of Chemical Analysis," 1927, Vol. 1, 558.
19 Johnson, C. M., " The Determination of Tungsten and Columbium in Stainless Steels," *Iron Ag*, April 11th, 1946, **157**, No. 15.
20 Schoeller, W. R., and Jahn, " The Analytical Chemistry of Tantalum and Niobium," 1939, p. 86 and 49, and Chap. 2, p. 14.
21 Hillebrand, W. F., and Lundell, G. F., "Applied Inorganic Analysis," p. 551.
22 Lundell, G. F., " Chemical Analysis of Iron and Steel," 1931, p. 330.
23 Schoeller, W. R., " The Analytical Chemistry of Tantalum and Niobium," 1937, p. 102.

24 Lundell, G. F., Hoffman, J. I., and Bright, H. A., " The Chemical Analysis of Iron and Steel," 1931, p. 364.
25 *Ibid*, p. 74.
26 Box, F. W., " The Determination of Small Amounts of Aluminium in Steel," *Analyst*, July, 1946, **71**, pp. 317–19.
27 Schoeller, W. R., " The Analysis of Ores and Minerals of the Rarer Elements," p. 90.
28 Lundell, G. F., Hoffman, J. I., and Bright, H. A., " The Chemical Analysis of Iron and Steel," 1931, p. 41.
29 Private Communication.
30 Schoeller, W. R., " The Analytical Chemistry of Tantalum and Niobium," 1937, par. 38, p. 81.
31 *Ibid*, p. 84.

4. (b) The alkaline (sodium carbonate) fusion procedure should provide, by virtue of the almost complete insolubility of sodium niobate in the presence of high sodium ion concentrations (when filtered under the same conditions), a practically full yield of the hydrated earth acids, if acidification of the niobates is followed by ammonia precipitation, etc.[32] The tungsten in the filtered solution, when suitably concentrated, might be collected by the tannin-cinchonine procedure. (See method 5).

4. (c) Of all the procedures tried for separating tungsten the sodium chloride[33] procedure gave most accurate results (in 1938), but it was not necessary to use it in routine as tungsten was not present in steels analysed here after that date ; and, even before that date, only in small amounts, and then G. S. Smith's procedure was used as it was speedy.[13]

E. J. Harpham[4] has apparently confirmed this by his work for this procedure for steels ; but it would be interesting to know (as he does not use sulphurous acid which induces quicker precipitation of tungsten[34]) why he does not hydrolyse the niobium by a boiling operation. Note that tartaric hydrolysis[35] involves a boiling operation and niobium must be *wholly* precipitated. The writer agrees, from his own experience, that not all the tungsten is precipitated. If up to 0·6% tungsten is present in the steel, probably two-thirds only of the tungsten is precipitated. In E. J. Harpham's procedure it is observed that caustic soda apparently removes silica from the residue of niobium pentoxide by reason of the fusion of silica with the alkali forming soluble sodium silicate.

5. The ordinary soda separation used in the lead molybdate procedure for the determination of molybdenum in steel may be used for the determination of tungsten, in the absence of molybdenum. In aqua regia solution of 18/8 Ni-Ta-W steels some refractory carbides remain insoluble in the acid mixture and may be filtered off and fused with potassium bisulphate. The combined main and extracted solutions are concentrated to a volume of 50 mls., and this solution is then added to one of 20 g. of caustic soda in 200 mls. of water. At about boiling temperature, this provides, in the writer's experience, an excellent separation of molybdenum from niobium. Tungsten and molybdenum may, if present, possibly be jointly precipitated, from the filtrate using lead molybdate as a reagent but a 2% sulphuric acid solution of these elements is easily obtained and is saturated with sulphuretted hydrogen for half an hour, followed by a slight increase in the acidity, etc. This procedure[36] is capable of yielding excellent results, even for 18/8 Nb-Ta-W-Mo steels, as the niobium is not an interfering element, having been collected with the precipitated iron hydroxide.

If niobium were present in the filtered soda solution, free of iron and chromium, it would be revealed in the lead molybdate procedure : as upon acidification with hydrochloric acid, followed by boiling for ten minutes or less, the niobium would be hydrolysed. [Even if it were present the expedient of dissolving molybdenum oxide in warm 50% ammonia (Johnson[36]) will reveal the presence of iron and niobium in practice, if in significant amounts]. Ammonium acetate would tend to

collect the niobium pentacid with the lead molybdate ; and niobium is *not* present in final lead molybdate residues. Spectrographic tests confirm this point. This method gives more reproducible results here than the spectrographic methods for FMB steels. In attempting to utilise for a determination of niobium the soda insoluble fraction of the molybdenum determination one is met with the necessity of thoroughly washing the precipitate with a 1% soda solution, and also the necessity for a reprecipitation of the soda insoluble precipitate, etc. In routine work, fractional separation is resorted to, which saves time and this is a welcome practical help. If time is available, the insoluble fraction, containing iron, nickel, chromium, cobalt, niobium, tantalum and (probably) copper obtained as above may be redissolved in hydrochloric acid and then T. R. Cunningham's procedure may be applied to determine niobium, now separated from tungsten and molybdenum. In determining tungsten by this or alkaline methods, it is necessary to boil down the solution to a low bulk and to use tannin and cinchonine.[37]

Determination of other metals.—Nickel is determined by the usual dimethylglyoxime method. The procedure of F. W. Haywood and A. A. R. Wood[38] for the determination of cobalt is applied here by dissolving 0·1 g. weight of sample in aqua regia mixed with the requisite amount of Spekker acid for a 3 mls. fraction of the main solution to be treated exactly as in the above procedure. Reproducible results are obtained here. Fractions have to be varied, in practice, to suit various ranges of percentages of cobalt.

The chromium determination as made by following the permanganate or Vignal method yields the most accurate results ; but an analoid persulphate procedure (No. 35), using sodium nitrite reduction and an oxidation indicator, was combined with the solvent and volume of solution used in the method developed for high nickel chromium steels in America[39] ; and yields excellent results here in this form, even for low alloy steels.

If tin is known to be present a distillation procedure is needed.[12]

Copper has been determined here with cupferron on an aqua regia solution which has been " taken to fumes " with sulphuric acid. Some alloys require an evaporating dish for this purpose and 0·5 g. weight of sample is the recommended maximum weight advisable in practice. *Copper* may be determined by cupferron precipitation[40] jointly with titanium, iron and niobium. Copper is removed from the precipitate (a) by washing it with ammonia and water. Reacidification of the filtered solution with acetic acid in very slightly acid conditions reveals copper as a cupferron salt. (An excess of fresh cupferron solution may be added, and this itself removed from the filtered precipitate by washing it with a 1% solution of sodium carbonate. Methods involving the destruction of cupferron are not advisable. Ignition of the precipitate followed by solution of the residue in nitric acid enables one to introduce the sodium carbonate neutralisation operation preceding the iodide volumetric method for the determination of copper. Iron and niobium, etc., may be determined on the residue obtained from (a) after washing with ammonia and water, ignition, etc.

32 *Ibid*, p. 15.
33 Schoeller, W. R., " The Chemical Analysis of Tantalum and Niobium," 1937, p. 88.
34 Lundell, G. F., " The Chemical Analysis of Iron and Steel," p. 328.
35 Schoeller, W. R., " The Chemical Analysis of Tantalum and Niobium," 1937, p. 57.
36 Johnson, C. M., " The Chemical Analysis of Special Steels," 1931, pp 155–157.

37 Schoeller, W. R., " The Analysis of Ores and Minerals of the Rarer Elements," 1940, p. 211.
38 Haywood, F. W., and Wood, A. A. R., " The Determination of Cobalt in Ferrous Alloys," *J. Soc. Chem. Ind.*, March, 1943, *XLII*, 37–39.
39 Scott, W. D., " Standard Methods of Chemical Analysis," 1939, **2**, p. 1,456.
40 Scott, W. D., " Standard Methods of Chemical Analysis," 1927, p. 746.

Direct sulphide and thiosulphate procedures applied in dilute sulphuric acid solutions involve a little iron being present in the precipitate of copper sulphide and require that the precipitate be washed with sodium sulphide to remove molybdenum sulphide before the volumetric copper determination may be made. Molybdenum has not to be removed before thiocyanate methods for the determination of copper may be used successfully. Group 3 elements are precipitated by ammonia and occlude a little copper.[41] Large accumulation of ammonium salts do not help the determination of

moderate amounts of copper in the filtrate, however, by the Iodide method. Precipitation of copper as a metal by aluminium foil is not suitable as iron is also precipitated,

Selenium.—This is satisfactorily determined by the method given for the analyses of stainless steels used by Carpenter Steel Corporation, U.S.A.[42]

Acknowledgment is made to the Directors of Murex Welding Processes, Ltd., for permission to publish this article and to E. C. Rollason, M.Sc., Ph.D., for his interest in the work.

41 Lundell, G. F., and Knowles, H. B., *J. Amer. Chem. Soc.*, 1923, **45**, 680.

42 Carpenter Steel Co. Scott, W. D., "Standard Methods of Chemical Analysis, **2**, 1,480.

National Association of Corrosion Engineers

THE above Association recently held its 1948 Conference at St. Louis, at which an extensive technical programme was presented comprising symposiums on the oil industry, water industry, chemical industry, electrical industry, cathodic protection, protective coatings for metals, general industry, communications, salt water corrosion, and the gas industry.

Dr. Ulick R. Evans and Dr. John M. Pearson honoured

Two eminent research authorities received the 1948 awards of the Association : the Willis Rodney Whitney Award in Corrosion Science to Dr. Ulick R. Evans, and the Frank Newman Speller Award in Corrosion Engineering to Dr. John M. Pearson. These awards are made annually by the N.A.C.E. in recognition of outstanding contributions in science and engineering appertaining to the field of corrosion. Dr. Evans was honoured in recognition of his outstanding contributions to the fundamental knowledge on which the practical control of corrosion is based. Dr. Pearson's award was for outstanding service in the application of scientific research in the prevention of corrosion, particularly by cathodic protection of underground structures.

Dr. Evans has been engaged continously on scientific work at Cambridge University, mainly in studies of corrosion of metals, thin films on metals and recrystallisation changes in metallic structures. He has published approximately 180 papers, and, in addition to lecturing at Cambridge University, has delivered many lectures by invitation at various centres throughout the world. He is the author of several books on the corrosion of metals which have been published in many different countries. Probably his most important contributions have been his studies on the electro-chemical nature of corrosion, and the first quantitative measurements co-ordinating corrosion rates with the amount of electric current flowing during " natural " corrosion were made in his laboratory. Because of the extent, accuracy and clear presentation of the results of his work, Dr. Evans has been a great influence in the thinking of other workers in the field of corrosion.

Dr. John M. Pearson in 1930, was affiliated with the Production Department of the Sun Oil Company at Dallas, Texas, working on electrical geophysics. In 1931, he became associated with the Susquehanna Pipe Line Company, Philadelphia, Pa., as physicist. Subsequently he became chief engineer, and in 1943 was made manager and a director of the Company. He rejoined the Sun Oil Company in 1945, becoming director of its Physical Laboratory at Upland, Pa. At the present

time Dr. Pearson is the Director of the Physical Division of the Research and Development Depart ment of the Sun Oil Company. During the course of his affiliation with the Susquehanna Pipe Line Company he developed numerous methods and instruments for measurements in the control of corrosion. These included an instrument for accurate measurement of current potential and density along underground pipe lines ; methods for measuring efficiency of underground insulating joints ; a visual three electrode earth current meter for use in corrosion surveys, and the servo-type vacuum voltmeter which has found extensive application in corrosion measurements. He is the author of a number of papers relating to underground corrosion.

Tube Investments acquires Crane Packing Ltd.

Tube Investments announces the acquisition of Crane Packing, Ltd., of Slough, Bucks, which specialises in the manufacture of heat exchanger tube packings, flexible and semi-metallic packings, insoluble lubricants, plastic lead jointing seals, flexible extractors, and tools for condenser packings. Plans are in preparation to extend output capacity to deal with increasing business resulting from the world dollar shortage.

Increase your Exports

The greatest urgency of many manufacturers in this country is an increase in the export of their products. Not only do they fully appreciate that on their combined efforts the future of this country's prosperity depends, but supplies of raw materials in many instances may be allocated conditionally upon the securing of extensive sales overseas, before it becomes possible to fulfil their obligations at home.

Exporting is a specialised job. Only very large manufacturers can afford to establish an export department to deal completely with their direct enquiries, but even so this is only half the battle and, incidentally, it can be a very expensive way of solving the problems involved. Those manufacturers interested in developing overseas markets will find a recently published booklet entitled " Export Advice " of more than ordinary interest. It describes the directions in which British Traders and Shippers, Ltd. can co-operate with manufacturers to increase overseas trade. This co-operation is supported by a wide knowledge of international trade, market requirements, shipping, insurance, licensing and many other problems associated with the export trade. A copy of this booklet is available on application to British Traders and Shippers, Ltd., Stevinson House, 155, Fenchurch Street, London, E.C. 3.

IT is gratifying to learn that there is a reasonable possibility of an increase in the amount of paper available for books. The lack of up-to-date text-books in this country has driven many lecturers to one of two courses, the recommendation of American text-books or the operation, themselves, as text-books, either through more detailed lectures or by the issuing of notes. Neither of these is satisfactory, or even adequate. At present, one is no surer of the availability of American text-books than one is in the case of the home variety. The second alternative is productive of a distressing waste of time. Lectures should perhaps be a gloss on text-books, an exposition of the lecturer's own ideas, a stimulation of the student's critical faculty or his powers of investigation. When they degenerate into the recitation of potted facts which should be available elsewhere, they no longer deserve the name of lectures. The system of issuing notes ancillary to lectures has its strong adherents, and has much to recommend it. But to have to provide notes which are not the product of the individuality of the lecturer, at the expense of much time and labour which in most cases could be spent much more profitably otherwise, is a part no teacher should be called on to play. The text-book problem can only be solved by increased paper supplies. It follows, then, that on these supplies depends the quality of the next generation of scientists.

The Microchemical Balance
Part V—Ancillary Apparatus*

By Cecil L. Wilson
Microchemistry Laboratory, Chemistry Department, The Queen's University of Belfast

To complete the list of apparatus to be used in conjunction with weighing procedures a selection of apparatus for drying, and subsequently for cooling weighing vessels, is described.

THE drying of vessels, particularly those containing precipitates, should be considered in conjunction with the ignition of boats, since the subsequent problems which such treatment raises are similar. Many different types of drying apparatus are available. Simplest of all is the use of an ordinary oven, or, better from the space point of view, the construction of a small one of similar pattern. For a number of purposes, the author found it possible to adapt a silica muffle from the normal-type muffle furnace as an oven, when it was difficult to get material for the construction of a more orthodox oven. The muffle was adapted as shown in Fig. 8. A tray was made from duralumin sheet, to slide in and out of the muffle. On this, apparatus to be dried was placed. A sheet of Uralite was cut to fit the front of the muffle, snugly but not tightly, and was drilled to take a cork, which in turn carried a thermometer. The whole was simply placed on a tripod, and heated by means of an ordinary Bunsen burner with the flame turned quite low and controlled by means of a screw-clip. This improvised oven took up little space, and once it had been set for any particular temperature, a surprising constancy could be achieved without any necessity for constant adjustment. It is not suggested that this is an ideal

* *Continued from page 275.*

arrangement, but it may suggest to individual workers ways in which materials to hand may be adapted for this purpose.

Small articles can be simply dried in heating blocks drilled appropriately. Two patterns in use by the author over a number of years, and primarily designed for other purposes, are quite suitable. The first, which was first devised for the heating of centrifuge cones in qualitative work, and for organic micro-preparative work, is a cylindrical duralumin block, $2\frac{1}{4}$ in. in diameter and $2\frac{1}{4}$ in. deep, drilled to a depth of $1\frac{1}{2}$ in. with six holes, of diameters: $\frac{3}{8}$, $\frac{5}{16}$, $\frac{1}{4}$, $\frac{3}{16}$, $\frac{1}{8}$ and $\frac{1}{16}$ in., evenly spaced around a central hole, $\frac{1}{4}$ in. in diameter, which holds a thermometer. The block, as shown in Fig. 9, is mounted permanently, by three stout brass wires, on a Bunsen base, from which the tube has been removed. The height of the flame is controlled by a screw-clip. Tubes of different diameters may be dried rapidly at any predetermined temperature. If desired, drying can be hastened by an air current, provided by suction, as shown in Fig. 10.

The second type of block is applicable to beakers, and was originally designed, in the form described here, for heating solutions in such beakers. It is found that beakers containing solid material can equally well be

dried in the block. As shown in Fig. 11, the block, which is made from brass bar of rectangular cross-section, stands on three legs* so that its base is $6\frac{1}{2}$ in. from the bench top. It has six holes bored in it whose diameter will depend on the size of beaker most generally in use. A seventh small hole, in the middle of the length of the block, but set back from the line of the holes so that it will not interfere with manipulation, takes a thermometer. There is a small variation in temperature from the centre to the outermost holes, and for precise work this should be determined, but for general purposes the variation is not significant.

The two sizes most useful are blocks 12 in. long, $2\frac{1}{2}$ in. wide and $1\frac{3}{4}$ in. deep, carrying six holes 1 in. in diameter and 1 in. deep, and blocks 6 in. long, $1\frac{7}{8}$ in. wide and $1\frac{1}{2}$ in. deep, with holes $\frac{1}{2}$ in. in diameter and 1 in. deep, these being suitable for semi-micro and micro work respectively.† It is preferable to have these blocks of brass or copper rather than of duralumin, because of increased stability. The blocks blacken as soon as they are put into use, but no inconvenience has been found to arise from this.

The well-known drier of Benedetti-Pichler,[9] used in conjunction with a heating-block, and suitable for the drying of precipitates held on filter sticks, is shown in Fig. 12. The filter stick is attached by rubber tubing to a plunger through which air is drawn. This enables filtered air to be sucked past the precipitate held on the walls of the beaker, and then through the precipitate on the filter stick and the filter stick itself, thus ensuring rapid and complete drying.

Fig. 8.—Improvised oven.

A modification of this apparatus[10] more conveniently prepared from readily available laboratory materials, is shown in Fig. 13. As can be seen, the principle is precisely the same, but the whole apparatus can be immersed in a water or other liquid bath for heating purposes.

For drying hygroscopic materials which can be heated in a platinum or porcelain boat, the drying tube[7] shown
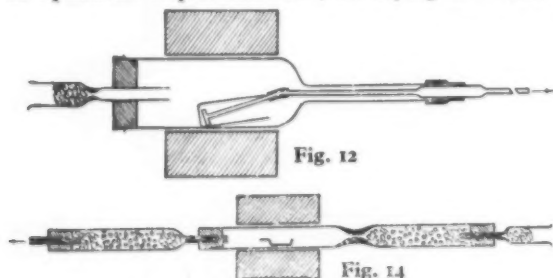
Fig. 12.—Benedetti-Pichler dryer.
Fig. 13.—Modified drier for precipitates.
Fig. 14.—Pregl drier.

in Fig. 14, which is heated in a metal block, is convenient. Its mode of operation will be obvious from the diagram, and drying is hastened by a filtered air current.

Two of the many types of so-called " pistol " dryers, for vacuum drying at elevated temperatures, may be

mentioned. A modification of the normal full-size pistol dryer is shown in Fig. 15, and consists of a jacketed tube, attached at the open end to a bulb which holds phosphorus pentoxide or other desiccant, by means of a ground joint. The tube is heated by the vapours from a boiling liquid bath. Provision is made for evacuation of the apparatus through a tap.

It is clear that the use of this is restricted to temperatures for which suitable boiling liquids are available. It is, therefore, much more convenient to use the simpler
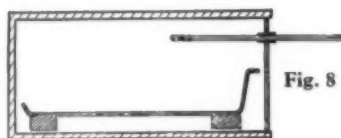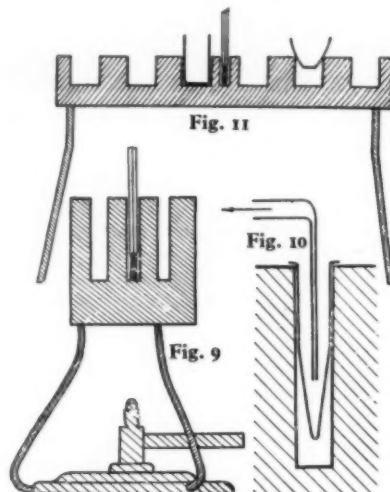

Fig. 9.—Small heating block.
Fig. 10.—Drying by suction.
Fig. 11.—Heating block for beakers.

modification shown in Fig. 16, which is merely inserted in a suitably bored metal block. If the diameter of this is made to correspond to that of the Benedetti-Pichler dryer mentioned earlier, the same block will serve for both pieces of apparatus.

Cooling of Apparatus

All apparatus to be weighed, whether it has been heated, or simply wiped, must be acclimatised, and for this purpose, small brass, copper or aluminium blocks are placed in suitable positions. At least one of these must remain permanently in the balance case, while several will be required within the outer balance case, just beside the balance. Articles can then be transferred to these for determined periods, before being finally placed on the balance pan for weighing. Such blocks are best set on small pieces of cardboard—to which they may be cemented — since otherwise they may acquire inconvenient temperature gradients if in direct contact with the balance table.

Fig. 13

For cooling articles which have been heated, before transferring to the acclimatising blocks, the apparatus often erroneously referred to as a micro-desiccator, is
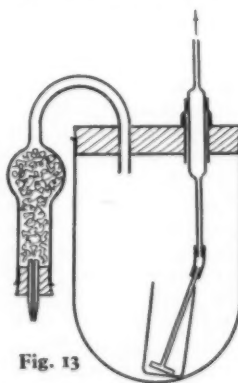
* Two at one end, one at the other end, to ensure that the block stands without rocking on any plane surface.
† In actual fact, once a block is constructed, further beakers are made to fit the block, rather than the reverse.
9 Benedetti-Pichler, A. A., *Mikrochemie*, 1929, *Pregl-Festschrift*, 6.
10 Wilson, C. L., *Introduction to Microchemical Methods*, Methuen, 1938.
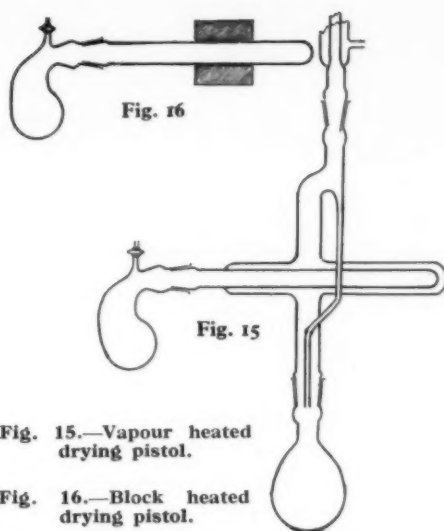
Fig. 16

Fig. 15

Fig. 15.—Vapour heated
drying pistol.

Fig. 16.—Block heated
drying pistol.

employed.[7] The original pattern, shown in Fig. 17, consisted of a copper block, supported on a metal framework inside a glass vessel with a ground-glass cover. This was of pre-war Continental origin, and has never, so far as the author is aware, been available in this country since 1939. Various expedients have been devised to replace this useful piece of apparatus. Saschek[11] has proposed the block shown in Fig. 18. This is made in two parts, so that the aluminium base can

be used for crucibles, or, together with the second cylindrical copper block (which has a slightly concave surface) for other types of apparatus. A glass cover. rests on the base. This can be a 50-ml. crystallising dish.

The author has found the block shown in Fig. 19 quite satisfactory. The circular base, of wood, is $3\frac{1}{2}$ in. in diameter and $\frac{3}{4}$ in. deep, and its upper surface is countersunk to a depth of $\frac{1}{4}$ in. to receive a cylindrical brass, aluminium or stainless steel block $2\frac{1}{2}$ in. in diameter and $\frac{3}{4}$ in. deep.* Over this a 250-ml. squat-form beaker forms a convenient cover. Such a cooling block is adequate for most apparatus likely to be met with.† When the block is to be used for cooling platinum boats, the precaution is taken of facing the metal with a sheet of ignited asbestos paper. Although this may not be necessary, it does not slow down the cooling of the boat excessively, and it avoids undue contact of the heated platinum with other metals. Care must be taken to brush off any possible adherent asbestos particles from the base of the boat before weighing.

For absorption tubes, a wire frame[12] such as that often used as a penholder (Fig. 21) and fastened to a cardboard base so that it does not come directly into contact with the base of the balance case, is required.

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11 Saschek, W., *Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 491.

* The dimensions may be modified to suit those of the appropriate beakers available in laboratory stock.

† In this connection, although it may not be strictly germane, two modifications of this apparatus may also be mentioned. For storing beakers and other vessels at intermediate stages, a simple wooden base, varnished and with a 250-ml. beaker as cover, may be used. The pattern is shown in Fig. 20. Recently, the author has learned that other laboratories have been making a parallel use of plastic bases similarly designed and covered. These have the added advantage that if a suitable choice of plastic is made for resistance to chemical reagents, they appear, and indeed are, much cleaner after prolonged operation. Both types may be bored with holes to take apparatus which will not lie on the surface of the block.

12 Belcher and Godbert, *loc. cit.*

Fig. 17.–Original
pattern cooling
block.

Fig. 18.—Saschek
cooling block.

Fig. 19.—Simple
cooling block.

Fig. 20.—Simple
storage vessel.

Fig. 21.—Wire
tube-rack.

Modern Analytical Methods

A SERIES of papers dealing with Modern Methods in Analytical Chemistry was read at a recent meeting of the Chemologists Club held in the Chemistry Department, Marischal College, Aberdeen. Mr. L. M. Valentine was in the Chair. The papers were as follows :

THE DETERMINATION OF TRACE QUANTITIES
OF HYDROQUINONE
By W. I. Stephen

A method was required for the determination of traces of hydroquinone between the range 0.3–300γ. The hydroquinone was being used as an inhibitor in poly-

merisation experiments and methacrylic acid was also present.

A number of direct colour reactions was tried, but had to be rejected for various reasons. Finally an indirect reaction was exploited and gave satisfactory results. The solution of hydroquinone is treated with a dilute solution of ferric chloride in a buffered medium and reaction takes place leading to the formation of ferrous ions. The excess ferric chloride is then rendered colourless by the addition of pyrophosphate ion. Orthophenanthroline is added and the intensity of the colour formed by production of the ferrous complex is directly proportional to the original amount of

hydroquinone present.   Methacrylic acid has no effect on the reaction.

"SOME NEW INDICATORS AND PRIMARY STANDARDS"

By A. E. Nutten

Two methods have been used hitherto for locating the end-point in bromate titrations. An irreversible indicator such as methyl red or indigo carmine is added and when the end-point is reached the indicator is irreversibly bleached by the free bromine formed. Alternatively excess bromate is added, followed by potassium iodide and the liberated iodine titrated using standard thiosulphate. The irreversible indicator method is unsatisfactory as local concentrations of free bromine occur and the indicator is bleached before the end-point is reached.

Two new indicators for this process which are reversible have been recommended a-naphthoflavone and ρ-ethoxychrysoidine and their use should simplify the bromate titration appreciably.

Starch indicator used in iodometric and iodimetric titrations has several disadvantages. It is insoluble in water, it is unstable and the end-point drifts in dilute solution. Recently a new indicator, sodium starch glycollate, has been recommended which is readily soluble in water, is stable and does not give drifting end points. It may also be added at the beginning of the titration since the iodine complex is water soluble.

The two indicators, ortho-phenanthroline and a, a^1-dipyridyl, have a variety of uses and their high sensitivity has been applied with advantage to a number of oxidimetric titrations. They have several other applications, for they can be used as colorimetric or complexing reagents.

Several new primary standards are now available for acidimetry and alkalimetry, but there are conflicting opinions concerning their reliability. This is particularly true of the organic primary standards. Probably the best modern primary standards which have stood the test of time are sodium borate as an acidimetric standard, potassium bi-iodate as an alkalimetric standard and potassium hydrogen phthalate as an alkalimetric standard in titrations using phenol phthalein.

Until recently there was no oxidimetric standard available incorporating the ferrous ion, owing to the difficulty of preparing stable or formula-pure ferrous salts. Recently, ferrous ethylene-diamine sulphate has been proposed and experiments carried out in this department show that it is an excellent primary standard. The solution is also stable. It has a high equivalent weight and simplifies the standardisation of permanganate and sulphato-cerate solutions.

A number of other organic ferrous complexes have been synthesised by the author, but only one other stable compound has been found, the homologous ferrous propylene-diamine sulphate. This compound behaves similarly to the ethylene-diamine complex.

"SOME NEW REAGENTS AND METHODS"

By L. Sabiston

The use of the silver reductor has simplified the determination of a number of elements, normally determined by oxidimetric processes. The advantage of the silver reductor over the Jones reductor is its greater selectivity. When the silver in the reductor is nearly all converted to silver chloride it may be readily regenerated by reduction without unpacking the column. Lead reductors may also be used with advantage.

8-hydroxyquinoline has now become established as a valuable analytical reagent for it not only provides a convenient weighing form but can be used for many separations by complex formation and control of pH. More recently 8-hydroxyquinaldine, which possesses greater selectivity, has been recommended. Magnesium and zinc may be separated from iron and aluminium, and by suitable adjustment of pH quantitative separation of magnesium and zinc may be effected.

Some few years ago manganic sulphate was recommended as a new oxidimetric reagent. It acts as its own indicator and has several advantages over permanganate. For example, it may be used to titrate solutions containing chloride ions. Unfortunately, it is unstable and its solution decomposes within an hour, hence, it has never been adopted.

Work has been carried out in this department with the object of stabilising the trivalent manganese by complex formation and it has been found that formation of tri-dihydrogen pyrophosphate-manganiate provides a stable solution. The reactions of this new reagent are identical with manganic sulphate.

A simple and efficient method for the separation of phosphate ions in qualitative inorganic analysis has been sought since the middle of the last century. Several methods have been devised, but all have some disadvantage and the basic acetate method, which always gives trouble in the hands of elementary students, is generally preferred. The author, in collaboration with A. E. Nutten, has recently worked out a method in which the phosphate is separated as titanium phosphate. It is rapid and efficient. Students who had been taught both this method and the basic acetate method and then allowed a free choice of methods, invariably chose the new method. It has now been adopted in this department as the standard method for phosphate separation in the teaching courses.

Microchemistry in Germany

The progress of microchemistry in Germany throughout the recent war was studied last summer by a team of British observers, and their findings have now been made available to the public.[1] As far as could be determined, the advances of interest were limited in scope, being primarily concerned, in the first place, with organic analysis—carbon-hydrogen combustion technique and the like. Even within this field, the more important developments seem to have been concerned with making the processes automatic or semi-automatic, though it is noteworthy that even of the German microchemists some realised that automatic procedures are only applicable with advantage where the substances to be analysed are closely standardised ; where a variety of substance-types are handled, individual treatment is still essential.

Little of interest to the inorganic chemist was discovered, the indications being that such advances were more likely to be found in Austrian laboratories.

The report is amplified by reproductions of a number of papers, mostly from Mikrochemie, concerning the developments quoted.

1 *Progress in Microchemistry in Germany.* B.I.O.S., Final Report, No. 1606, 1948.

French Colonial Mineral Wealth
By Pierre Legoux

THE vast extent of the French overseas territory, especially in Africa, is perhaps not generally realised and still less its very considerable mineral resources. Hitherto, attention has been directed mainly to agricultural and forest development, except in one or two localities where mining is the principal interest ; but in view of the supreme importance of metals in world economy to-day, serious efforts are contemplated by the French government, under the Monet plan or otherwise, to establish a more balanced regime in these territories, including both mining and manufacturing industry.

Some of the possibilities are reviewed by Legoux, who notes among others the nickel ores and chromate of New Caledonia ; lead and zinc ores of the Middle Congo ; cassiterite (tin) of Indo-China and the Cameroon ; wolfram and calamine (zinc) of Tonkin ; iron ores in Conakry (French Guinea) and New Caledonia ; bauxite in Guinea and Senegal ; copper in the Middle Congo, Madagascar, etc. Both solid and liquid fuel are apparently not lacking in some of these countries— coal in Tonkin and Madagascar, and possibly also petroleum in the latter and in Gaboon where promising trial drillings have been made.

Only a few of the above are selected for discussion, the first being chromite in New Caledonia where both the richer ores (more than 48% chromium trioxide) and also the lower grade for refractories are to be found in considerable abundance. New Caledonia is well situated for production of the different grades, especially the metallurgic in blocks or powdered concentrates containing from 46 to 55% chromium trioxide. The richest ores are found in the Tiebaghi and Chagrin areas, in which the chromium/iron ratio is from 2·9 to 3·3. Pre-war, production was about 55,000 tons per annum ; this was well maintained and sometimes exceeded during the war. In 1945, output was 60,000 tons.

Chromite is also found in Madagascar, Indo-China, and Togoland, but up to the present apparently the deposits have not been worked. In the Tamatave deposits (Madagascar) chromium oxide content is down to about 40%, but iron is higher (15–18%) and some alumina is also present (18–19%). The chromite of Than-hoa in Indo-China is somewhat similar but with more chromium and less of iron and alumina.

Titanium ores, both ilmenite and rutile, are found in French oversea territory. The ilmenite of Senegal (double oxide of iron and titanium) is mostly located in the Petit Cote, to the south of Dakar, and in Casamanca. Output (in 40% sand concentrate) in 1938 reached 8,400 tons ; this fell to 4,300 tons in 1939 ; varied considerably down to zero during the war ; and in 1945 was 2,460 tons. Following are analyses of two areas :—

	Rufisque	Casamanca
Titanium dioxide ..	55·8	58·9
Ferric oxide Fe_2O_3 ..	32·4	32·9
Ferrous oxide FeO ..	9·3	7·5
Misc.	2·5	0·7

In addition to the sand concentrate, some 56% ilmenite was produced to the extent of 1,056 tons in 1940, and 740 tons in 1945.

Rutiles in the Cameroon, sold on the basis of 95% oxide content, reached an output of 3,000 tons per annum in some war years.

In the ilmenite sands of Senegal is also found the mineral zircon, or silicate of zirconium, used in refrac-

tories and ceramics ; and there are appreciable amounts available in Madagascar.

The author also refers to columbo-tantalite, an amorphous mixture of iron niobate and tantalite. Niobium, which is another name for columbium, is always associated with tantalum, which it closely resembles. Both columbite and tantalite, its chief minerals, are mixtures of iron and manganese niobates and tantalates. It was of considerable interest to the Allies during the war, but its discovery in the Middle Congo was too late to be of much use then ; and the first consignment of a few tons of the ore have only lately arrived in France. As is well known by now, tantalum is used in electronics (radar) and in the form of very hard carbides. Both tantalum and niobium are highly resistant to corrosion, and the former—as double fluoride of tantalum and potassium— is employed as catalyst in synthetic rubber production. These ores are found also in Madagascar and the Cameroon.

In Le Grand Ile (Madagascar) which has an amazing variety of mineral wealth is to be found the mineral uranium—so important in nuclear physics and as a source of radium. The ore is a mixture of betafite (niobotantalate of uranium and calcium) and euxenite (niobotitanate of uranium and calcium). It is also found as the double phosphate in autunite.

Reference is finally made to cerium ore, e.g., monazite, for which Madagascar and French Equatorial Africa are said to be possible sources.

New Uses for Industrial Gases in the Production and Finishing of Steel Products

AMONG the important research activities being conducted by Air Reduction Company, in their new research laboratory, are those concerned with new uses for the industrial gases in the production and finishing of steel products. At a recent inspection of this laboratory, demonstrations were given of a number of processes, including cutting of hot steel billets with the oxy-acetylene flame, the use of industrial gases in steelmaking operations, the new method of scarping stainless steel, heliwelding of non-ferrous metals, and machine gas cutting with an electronically controlled tracing device.

Perhaps the most important of the industrial gas applications involves the use of oxygen as an aid in the combustion of fuel in steel melting and the control of hot metal analysis. Test work conducted with open hearth furnaces indicates that the relatively long period involved in melting down steel scrap may be shortened as much as 40%. Experimental work is also continuing in the use of oxygen in the foundry cupola and in the Bessemer convertor. Problems also being studied involve the manufacture of large volumes of low-purity oxygen and in the use of oxygen in the blast-furnace.

A more recent application for oxygen is the cutting of hot blooms and billets. The usual steel mill practice is to cut hot blooms mechanically with a shear. In view of the high cost of shearing mechanically, replacement of hot-shears with oxygen cut-off machines appears to be attractive. However, the economy of the substitution is contingent upon the ability to make cuts at speeds approximately those of the shear, and efforts are being directed to speeding up the oxyacetylene-cutting process.

The use of industrial gases for refining metals has advanced in recent years. The injection of oxygen into the molten steel bath of the open-hearth furnace, to bring about rapid carbon reduction, is said to raise production about 25% compared with the slag-metal practice. Already oxygen has become a regular production tool for plants making low-carbon steels. Flushing various metals with other gases, such as nitrogen, helium, and argon, has been found beneficial in eliminating certain physical defects, which might otherwise occur in the solidified product, such as porosity, poor grain structure, brittleness, etc.

Surface imperfections which develop in the casting and subsequent rolling of steel must be removed in order to obtain a quality product. In the case of ordinary steels this has been done by scarfing, a process in which a thin layer of surface material is removed by an oxy-acetylene flame. Until recently, this process was not applicable to the stainless steels because of the refractory nature of the oxides formed and it was necessary to remove defects by chipping and grinding, an expensive and time-consuming measure. The scarfing of stainless steels is now reported to be possible through the use of a flux, which has the property of reducing the melting point of the refractory oxides formed, so that the

oxidising action can be generated. The flux is injected into the oxygen stream and passes through the flame, coming into intimate contact with the metal being scarfed.

Of importance also, has been the development of inert-gas applications, using nitrogen or hydrogen as a base, for the protection of metals during heat-treating. In the manufacture of tin plate for the canning industry, in the production of high-silicon transformer steels for the electrical industry and in the making of high-grade alloy steels for the automotive industry, protective atmospheres are playing an increasing role in improving product quality.

Although the idea of shielding a welding arc with an inert gas is old, it attained commercial importance during the war years in meeting the urgent need for a better method of welding magnesium, aluminium, and stainless steel. Research work on the heli-welding process has demonstrated its remarkable versatility for fabricating most of the ferrous and non-ferrous metals and alloys which hitherto have been considered difficult to weld.

The Flash Welding of Structural Aluminium Alloys
By R. M. Curran and R. C. Baker

THE flash welding of 14S, 24S, 52S, 53S, 61S and Alclad 75S aluminium alloys in the 0·125, 0·188 and 0·250 in. gauges was investigated. Specimens 2 in. wide were used throughout the investigation. Weld quality was evaluated on the basis of tensile tests made using the as-welded specimens as well as standard machined specimens. A limited number of tensile impact tests were made of the flash-welded joints and hardness traverses were taken across the weld zones.

The flash-welding characteristics of the above alloys were studied in both the age-hardened and annealed conditions except in the case of 52S which was studied in the half-hard and annealed tempers. In addition to testing the flash welds in the as-welded condition several tensile tests were made of welds which had been furnace heat treated after welding.

As a result of this investigation two relatively new concepts have been introduced, the first of which is the use of three-stage heat control during the welding cycle. With three-stage current control, butting can be avoided during the remainder of the flashing cycle and the extent of over-ageing due to upset current flow can be reduced. The second concept is the use of much greater upset travel distances for aluminium alloys than is the practice in flash welding other materials. This procedure appears necessary in the flash welding of aluminium alloys if the oxide formed during the flashing cycle is to be eliminated from the final weld line.

The results of this investigation indicate that flash welding is a suitable means of fabricating 14S, 24S, 52S, 53S, 61S and 75S alloys. Although high-tensile joint efficiencies were obtained in the O tempers of these alloys the welds were not considered satisfactory since photomicrographs showed the presence of oxide in the weld line. This was further substantiated when welds made in the annealed material were age hardened after welding. These specimens showed relatively low joint efficiencies because the heat treatment could not affect the strength of the oxidised weld line.

In general it has been found that higher weld strengths can be obtained by welding the hard tempers of the aluminium alloys than by welding in the annealed condition. Joint efficiencies exceeding 90% can readily be obtained in welds made in the hard tempers and, if desired, full sheet strength can be obtained by heat treating after welding.

Experiments conducted on the 52S alloy in the ½H condition show that the work-hardened materials have the same flash welding characteristics as the aged tempers of the heat treatable alloys. Tensile impact joint efficiencies of welds made in 24S–T, 53S–T and 52S ½H using the welding conditions presented in this report were found to be higher than those of welds made in 14S–T, 61S–T and 75S–T. Joint efficiencies in tensile impact were considerably lower than would be expected in view of the high tensile joint efficiencies obtained. The type of tensile impact specimen which was used, however, considerably exaggerated the effect of softening in the weld line due to over-ageing.

Hardness surveys across the welds made in the age-hardened temper of the alloys indicate that the strength of these welds depends on the work hardening as well as the over-ageing properties of the material. In some cases, it appears possible to counteract the softening of the weld zone due to over-ageing by cold working the weld zone during the upset portion of the welding cycle. This further emphasises the important role of upset travel in the flash welding of these alloys. The need for an investigation of the thermal cycles and temperature gradients associated with the flash welding process has been demonstrated and experimental research designed to procure this type of information is now being conducted.

Powder Metallurgy

ADVANCES in the science of powder metallurgy have long been hindered by the difficulty of obtaining reproducible results in large-scale manufacture. This is due principally to present methods and techniques which introduce numerous variables as yet not completely understood or controllable. In conjunction with the current programme of standardisation of test methods and techniques in this field, the National Bureau of Standards undertook an extensive investigation of the conditions contributing to the lack of reproducibility in sieve analysis of metal powders. Such analyses of particle-size distributions are of major importance in powder metallurgy.

Investigations at the Bureau revealed that atmospheric humidity has a marked effect on the results obtained by sieve analyses of metal powders and that controlled atmospheric conditions during sieve testing of metal powders may therefore be necessary when close control of particle size is desired. Increase in humidity tends to increase the weight of the fractions retained on the sieves and decrease the weight of the pan fraction. Differences of as much as 10% between the weight of fractions of powdered iron sieved under high and low humidities have been observed.

In sieve tests of sponge iron, electrolytic iron, electrolytic copper, and nickel, made for the purpose of accumulating supplies of sieved fractions of these powders for other studies, it was found that reproducible results could be obtained only when certain variables were controlled. Significant

differences in sieve analysis often were obtained when samples of the sieve powder were sieved at different times with the same sieves. Furthermore, different sets of certified sieves used for the same powder gave variations of considerable magnitude. A contributing factor, in addition to atmospheric humidity, was a cumulative sampling error that resulted from repeated riffle cutting of limited powder supplies.

High Temperature Furnaces

A SERIES of extremely high-temperature research-laboratory furnaces has been announced by the Westinghouse Electric Corporation recently. One is capable of producing heats of 1,700° C., nearly 94° C. hotter than ordinary laboratory high-temperature furnaces. Also, it has an effective heat zone of about four cubic feet, which means it can take a charge approximately four times larger than is customary.

It is a radiant-type furnace, but instead of using heating elements consisting of fine wire coils wound on muffles, it uses less troublesome heavy molybdenum rod laid on ledges in the refractory brick. To produce these heating elements required molybdenum-to-molybdenum welds using atomic hydrogen, said to be its first application to large pieces of molybdenum.

Another research furnace of the same general dimensions and principle is expected to produce heats of 2,200° C.

A temperature of 2,600° C. is being sought in a still different, but much smaller furnace. In it a tungsten crucible, large enough to hold a walnut, is heated in an inert gas by a combination of radiant heat and high-frequency induction. Temperatures approaching 2,760° C. are really extreme. Tungsten itself begins to soften at about 2,700° C. These furnaces were built primarily for laboratory use. Commercial production is not planned for the near future.

High Temperature Metal

AN extremely hard metal that is said to retain its strength and resistance to corrosion at high temperatures has been developed by Kennametal Inc. of Latrobe, Pa. It is a special "cemented carbide" composition

manufactured by processes similar to those employed in making the carbides now used widely for cutting tools and wear-resistant parts, but with unique properties. Reports indicate that it withstands temperatures that rapidly destroy conventional carbides and the best cast alloys ; resists thermal shock much better than ceramics ; and has a specific gravity about one-third that of tungsten carbide and two-thirds that of steel.

Pieces of this composition, grade K138, are said to have been heated to 1,150° C. for 48 hr. without loss of strength. Neither does it change appreciably when heated to 980° C. and quenched in water. Air cooling from the same high temperature leaves no effect other than initial discoloration of the surface. Its unique properties suggest many practical uses. Resistance to oxidation and hot gases, together with abrasion resistance because of high hardness, make it suitable for high-temperature structures, such as furnace parts, and guides for hot-rolled metal. Its lightweight and strength are advantageous for rotating parts exposed to high temperatures.

This heat-resistant material consists essentially of titanium carbide with cobalt as the bonding element. The titanium carbide has heretofore been used only as a minor ingredient of cutting-tool alloys. The metal can be formed into a great variety of shapes and sizes, with tolerances and finishes common to conventional cemented carbides.

Die Materials for Casting Aluminium Alloys

IN a report and review of relevant literature by the Directorate of Research of the Technical Centre of the Foundry Industry, the properties of a satisfactory die material for casting aluminium alloys are listed. They include good machining properties, resistance to wear and deformation in mass production, low manufacturing cost and simple heat-treatment requirements.

A review of earlier work, together with references to papers and articles, is given in chronological order, and tables are shown of the various alloys proposed. Gravity casting and pressure casting are considered separately. It is concluded that the development of die materials depends largely on three factors : theoretical analysis

tested under laboratory conditions and aimed at giving the optimum qualities in accordance with the length of service required, manufacturing costs, and performance under practical conditions. In the latter are included the possibilities of maching the steel before heat-treatment without subsequent deformations and of quenching at a temperature low enough to facilitate the handling of heavy blocks. On the basis of these considerations the most suitable materials for gravity castings were found to be an ordinary, dense, grey cast-iron or a heat-treated cast-iron with a 2% chromium content. The best performance is given by a homogeneous, inoculated cast iron. For pressure castings a die of nickel-alloy steel can be used with tungsten-steel reinforcements at the more vulnerable points. Chrome-vanadium steel can also be used, or a chrome-tungsten steel with a high silicon content and containing molybdenum and possibly cobalt or vanadium. The latter is considered to be the most suitable material.

Low-Temperature Phosphate Coating for Steel

THE value of phosphate coatings for steel is well known, but there has been some restriction on the use of these coatings due to temperatures required by most processes. Now, however, there is available a cool-spray process known as Granodising which has several objectives and results. The action of the coating on metallic iron transmutes the surface into a layer consisting essentially of zinc phosphate. This protective integument is crystalline and non-

metallic and is integrated with the parent metal. The life of finishes over such surfaces is longer than on untreated steel.

The phosphate coating tends to suppress the destructive activity of galvanic action. Rust or corrosion is restricted to areas where accidental scratching, denting or chipping has exposed bare metal. The spread of rust or corrosion beyond the locale of damage is greatly inhibited and retarded by the presence of a phosphate bond under the paint finish.

It is in the actual process that Granodising differs most from other methods of treating metal surfaces. The most important factor is that it is done at bath temperatures not exceeding 120° F. Because of the small heat requirements steam costs are reduced. Heat is usually required only in starting up a cold washer. Heat transferred from a hot cleaning solution, mainly by condensation, plus heat present in the plant is sufficient to maintain proper operating temperature. In addition to saving on steam costs maintenance of steam coils is simple since the small quantity of scale which forms on them is powdery and can be brushed off readily.

The solution is maintained super-saturated by continuous additions of metered quantities of a primer. Controlled quantities of the accelerating agent, hydrogen peroxide, are maintained by metered additions of a toner. The zinc phosphate content is maintained by metered additions of the zinc phosphate solution, Granodine. Other advantages of the process include the fact that the solution does not give off rust stimulative vapours ; sludge formed in the process is soft, minimising clogged spray nozzles ; chemical costs are low and operation is economical.

A Metallurgical Study of German Aircraft Engine and Airframe Parts—Vol. II

IN fulfilment of a promise made to the Aero Components Sub-Committee of the Technical Advisory Committee, when the late Dr. T. Swinden was its Chairman, we are publishing the second and concluding part of the Report on German aircraft engine and airframe parts in book form, similar to the copy of the first part published in 1943 and reprinted in 1944. It will be remembered that, in the introduction to the first book it was stated the work included in that report embraced the results of investigations carried out from the beginning of the war until towards the end of 1941, but that the work was continuing. This new report about to be published embraces the results of the further investigations carried out.

The work covered by this report is really a summary of very extensive investigations which have been carried out meticulously and at great cost. Essential information arising from the study of components is presented in concise and readily assimilated form, and the text is supported by numerous illustrations which, in themselves convey valuable information to the initiated. Extensive tabulated data are also presented.

As in the case of Part I of this report, from the proceeds of which £500 has so far been credited to the Royal Air Force Benevolent Fund, we, the publishers, have agreed that the whole of the profits arising from the sale of Part II will be credited to the same Fund. In order that the maximum sum may become available for such a deserving cause, we are seeking orders for the book in advance of publication. This will enable us to estimate more accurately the number of copies needed before we go to press, and thus limit the number of surplus copies—a waste which would reduce the amount to be credited to the Fund.

The preparation of Part II of this book is well advanced but it is not yet possible to give a publishing date ; you may be assured however, that as far as we are concerned there will be no unnecessary delay and orders will be executed as soon as copies are ready. It will comprise about the same number of pages as Part I, and will be worthily bound. Although printing costs have risen since the publication of the earlier book, it has been decided to publish the new book at the same price, viz., 10s. 6d. net.
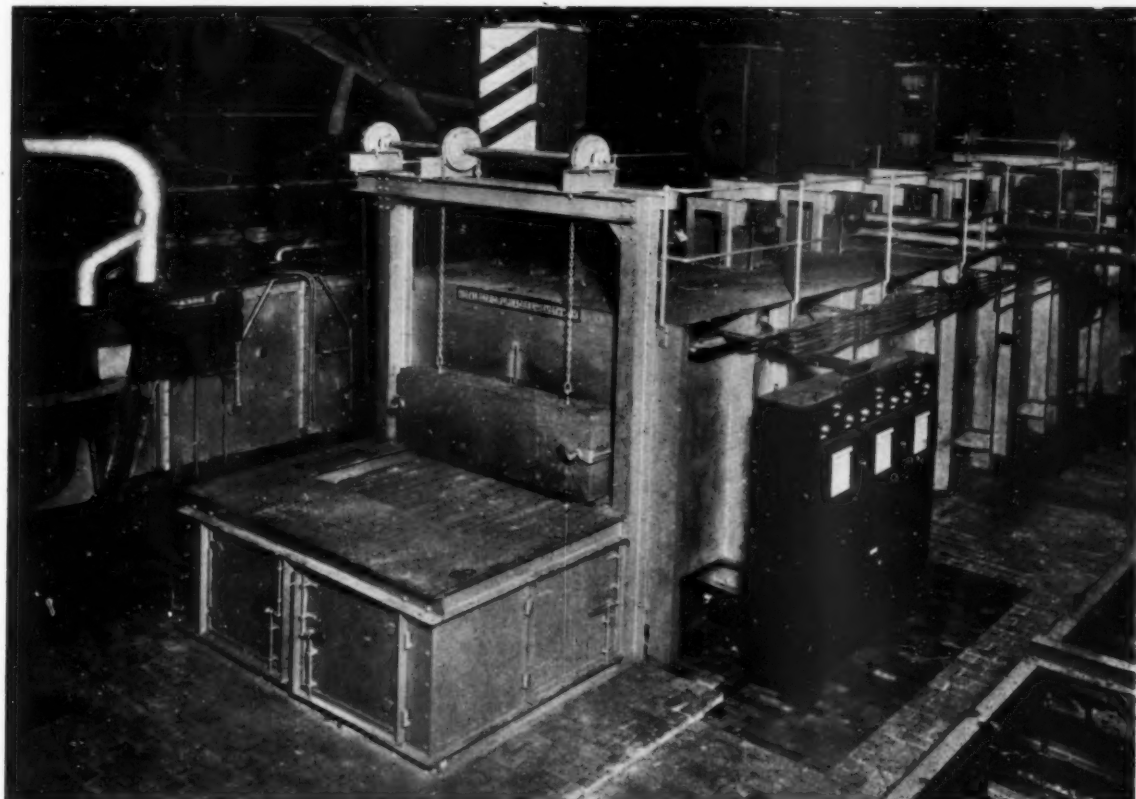
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